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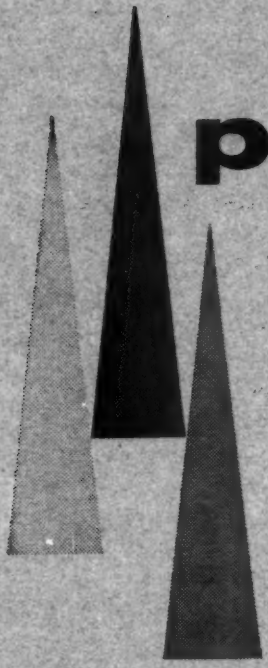

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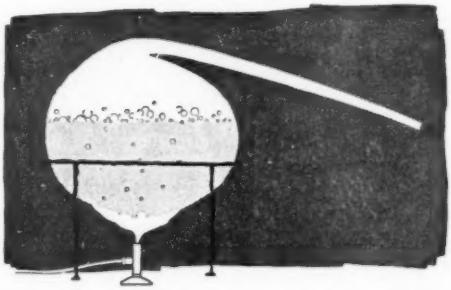

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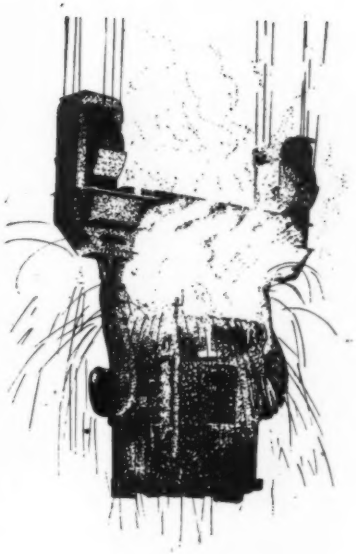

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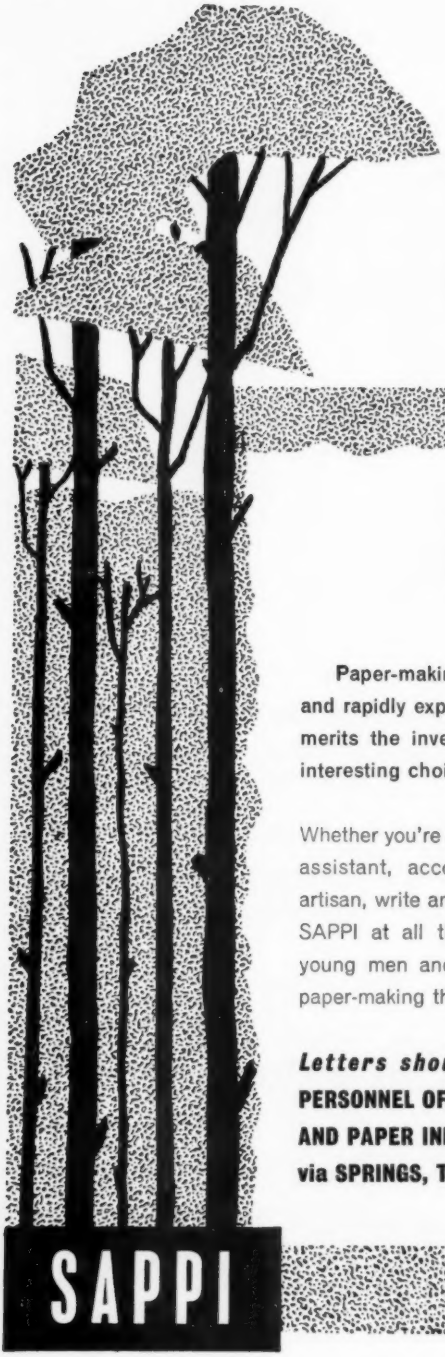

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THE DETERMINATION OF COPPER BY MEANS OF ATOMIC ABSORPTION SPECTROSCOPY*

by

A. STRASHEIM, F. W. E. STRELOW and L. R. P. BUTLER.

OPSOMMING

Die bepaling van koper in ertse, konsentrate en in ertsafal met behulp van atoomabsorpsie, word beskryf. 'n Vinnige ekstraksieprosedure om die kopererts ens. in oplossing te bring, met behulp van gemengde sure, maak die metode geskik vir produksiekontrole. Vir koperkonsentrasies wat varieer van 0·18 tot 24% is die noukeurigheid van die metode beter as 7%.

SUMMARY

The determination of copper in ores, concentrates and tailings by means of atomic absorption, is described. A rapid extraction procedure to bring the copper ores etc. into solution, using acid mixtures, allows the method to be used for production control. The accuracy of the method is better than 7% for copper concentrations varying from 0·18 to 24%.

INTRODUCTION

The use of atomic absorption spectroscopy for analytical purposes was revived by Walsh[1] and furthered by Russell, Shelton and Walsh.[2] Other authors[3, 4] have since been equally successful in developing analytical methods based on this principle. Atomic absorption spectroscopy, when used for analytical purposes, has certain advantages over other methods, viz.:

(*a*) It can be used for absolute determinations.[1]

(b) It does not require standards in the same physical condition, but does require that samples and standards should be in solution.

(c) It is not affected by self reversal or self absorption.

(d) The very stable hollow cathode excitation gives good accuracy.

These advantages suggested its use as a routine method for the analysis of copper in sulphide or silicate ores. Methods have been described for the estimation of copper by emission flame-photometry,[5] but they have the inherent difficulties experienced with this type of analysis. In this paper a method is discussed for using atomic absorption spectroscopy for determining copper in solutions prepared from ores, concentrates or tailings.

EXPERIMENTAL

Apparatus. A Hilger and Watts Uvispek spectrometer together with atomic absorption attachments, was used.

The jet in the water-cooled burner was replaced by one having a 0·027 inch diameter hole to enable it to be used with Handigas fuel. It was found that if tap water was used to cool the burner, this became too cool and vapour condensed on the lower face, causing contamination and less efficient vaporisation. These difficulties were overcome by circulating water from a 5 litre reservoir through the burner top

*A paper read in Stellenbosch at the Fourteenth Annual Convention of the S.A. Chemical Institute on February 11, 1960.

by means of a Stuart-Turner centrifuge pump. During use, the temperature of the water rose to approximately 60°C and then remained constant. The burner was positioned approximately $\frac{3}{4}$ inch below the optical axis. This position was found by adjustment of the burner height to obtain maximum absorption.

The performance of the spectrometer was appreciably improved by stabilising the mains supply to the hollow cathode and Uvispek power supplies with a Wandel and Golterman voltage stabiliser.

Principle of the method. The principle of the method has been fully described by Walsh and others [1, 2, 3, 4] and will only be briefly mentioned here. The light from the cathode passes through the flame into the spectrometer which is set at the wavelength of one of the resonant lines of copper, viz. 3247Å. If now a solution containing copper is sprayed into the flame, sufficient heat is available to break up the solution into an atomic vapour. A large number of free neutral copper atoms will then be present in and around the flame mantle. These atoms absorb the characteristic radiation of copper coming from the hollow cathode lamp, and the spectrometer measures the decrease in light intensity at this resonant wavelength.

General analytical procedure. In the atomic absorption method using the Uvispek spectrometer the analytical results are based on single absorption measurements. Constancy of the apparatus is, therefore, a stringent prerequisite. New analysis curves must thus be prepared when the instrument has to be used for a new analysis or a new series of analyses and standard solutions have also regularly to be sprayed into the flame to check the instrument. Readily available material for standards, which can easily be prepared, is thus a necessity. A primary standard solution for the preparation of the analytical curves and for checking the instrument was prepared by dissolving a weighed quantity of specpure copper in warm dilute hydrochloric acid. This solution was made up to volume to give a standard stock solution containing 1000 p.p.m. of copper. Further standards were prepared by dilution from this stock solution.

The general analytical procedure was as follows: After allowing sufficient time for the instrument to warm up, a series of standards was sprayed through the flame, the different density readings recorded and the analytical curve prepared (a typical curve is illustrated in Fig. 1). The solutions containing the unknown amounts of copper were then sprayed into the flame, the density readings recorded and the unknown concentration values read from the analytical curve.

It was found unnecessary to rinse the spray chamber after each solution, as fresh solution removed contamination within a few seconds.

The operating data of the instrument are given in Table I. The settings were found by adjusting all components to optimum conditions.

TABLE I

Standard analytical conditions

Element line	Cu 3247 Å
Slit	0·20 mm
Meter sensitivity setting	6
Air pressure	20 lb/sq inch
Handigas pressure	0·75 lb/sq inch
Sample consumption	20 ml/min
Anode current of hollow cathode	40 mA

(*a*) *Factors affecting atomic absorption results.*

(i) *Influence of gas and air pressures.* The temperature of the flame is not very dependent on the air pressures applied to the atomiser (varying from 15 to 30 lb per

square inch). For air pressures above 30 lb per square inch the angle of the curve is lowered as is illustrated for a pressure of 35 lb per square inch in Fig. 2. Although 30 lb per square inch gave the steepest curve, a pressure of 20 lb per square inch was chosen as standard operating condition, because of the lower rate of sample consumption and the more reproducible results. The curves illustrated in Fig. 2 also indicate that low concentrations of copper are less affected by changes in pressure. This fact should be borne in mind when doing routine analysis. These results also suggest the use of two dilutions when determining unknown samples. In this way a check can be achieved on the results.

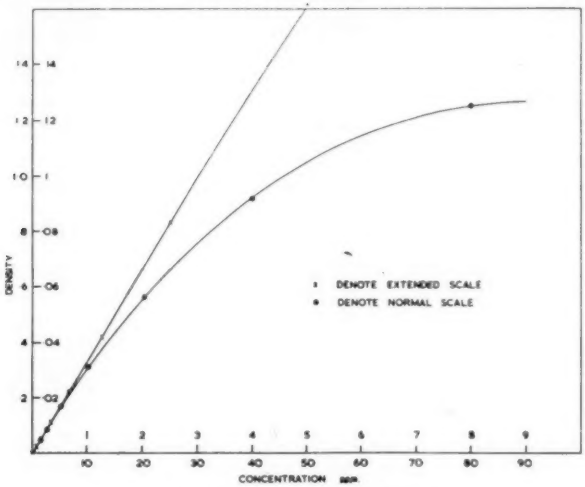

Fig. 1—Typical analytical curve

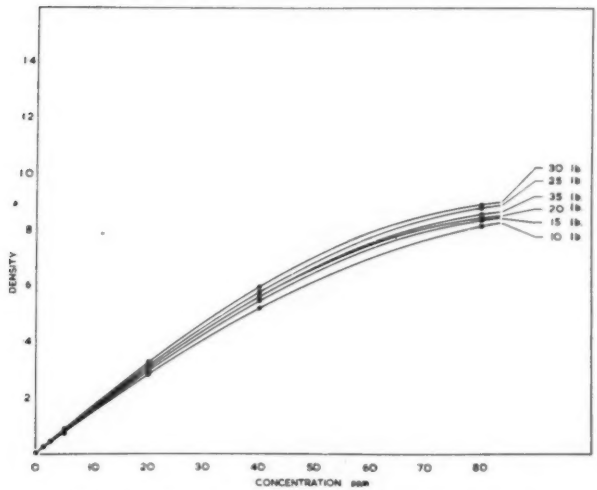

Fig. 2—Influence of air pressure on analytical curve

In contrast to flame-photometric spectroscopy[6, 7] where high temperatures are now preferred, the temperature of an atomic absorption unit should only be sufficient to vaporise the sample and dissociate the molecules into neutral atoms. When the gas pressure to the burner is changed from 0·25 to 1 lb per square inch, the total variation possible, the temperature increases from 950 to 1390°C. As no difference in the evaporation or dissociation of the copper molecules could be detected with variation in gas pressure, 0·75 lb. per square inch was chosen as the standard analytical condition.

(*ii*) *Influence of anode current of hollow cathode lamp on analytical curve.* Fig. 3 shows the effect of the anode current of the hollow cathode lamp on the analytical curve. The lower the anode current, the steeper and the more linear the analytical curve becomes. A decrease in the anode current results in a decrease in the cathode temperature. Under these conditions the copper line is narrowed and more effective absorption of the copper resonant radiation can be expected, as absorption occurs in a very narrow band of wavelengths.

The line intensity of the hollow cathode lamp is unfortunately related to the anode current and the sensitivity of the spectrometer limits the use of anode currents which are too low. These findings are in agreement with those of Allan.[3]

(iii) *Influence of extraneous elements and acids.* One of the drawbacks of flame-spectroscopy is that chemical combinations occur in the solution and in the flame. This prevents the atoms from coming into the flame in a free neutral form. In order to test the influence of extraneous elements, a series of solutions was prepared containing varying concentrations of Ca, Na, Fe, K, Al and Co, the elements most likely to occur as impurities in copper ores and associated materials. The influence of acids was also tested and the results in Table II show that no influence could be detected.

(b) *Procedure for the analysis of copper ores.* The success of an analytical method when used for production control generally depends on the "lapse of time" before results become available. A rapid extraction procedure to bring the copper ores etc. into solution was thus sought. Various methods of dissolving the samples were tried. The most successful acid mixtures to dissolve a 0·5 gram sample were, in order of merit:

(i) 10 ml 40% HF + 10 ml conc. HNO_3,
(ii) 10 ml conc. H_2SO_4 + 10 ml conc. HNO_3 and
(iii) 10 ml conc. HCl + 10 ml conc. HNO_3

The general extraction procedure is as follows: The samples are weighed and transferred to platinum crucibles. After adding the HF-HNO_3 mixture, the crucibles are heated on a hot plate. The solution is then transferred to a 200 ml volumetric flask and made up to volume. This solution is filtered, the first 20-30 ml discarded and the next 20-30 ml used for the analysis. If the copper content of this solution is too high, the necessary dilutions are made.

With some flotation samples a little black carbonaceous or sulphurous matter remained undissolved after the acid treatment. The amount of copper present in this residue was found to be negligible.

To determine the optimum extraction time, three samples containing 19·6, 27·5 and 30·64% copper were digested for varying times. The copper concentrations in the extracted solutions were then determined using the atomic absorption procedure. These results are shown in Table III. From these results it is evident that:

(i) for full extraction a digestion time of about 40-60 minutes is required,

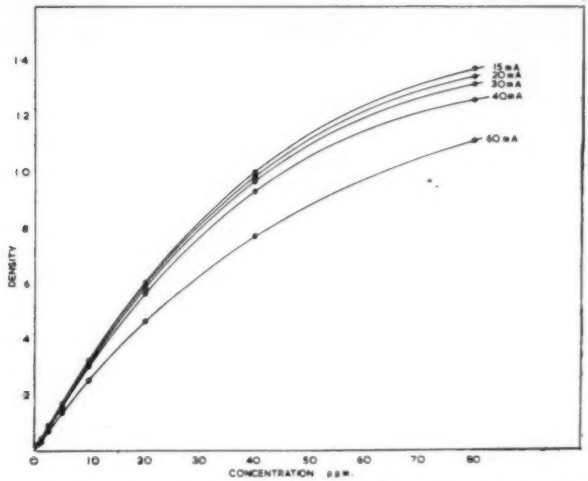

Fig. 3—Influence of anode current of hollow cathode lamp on analytical curve

TABLE II

Influence of other elements and acid radicals on results

Extraneous element or acid present in solution	Concentration present	Cu detected by atomic absorption, p.p.m.
Ca	0 p.p.m.	1·48
	1000 ,,	1·46
	10000 ,,	1·45
Na	0 ,,	2·5
	1000 ,,	2·5
	10000 ,,	2·4
Fe	0 ,,	1·57
	500 ,,	1·55
	5000 ,,	1·56
K	0 ,,	1·03
	1000 ,,	0·91
	10000 ,,	0·95
Al	0 ,,	1·25
	5000 ,,	1·26
	10000 ,,	1·26
Co	0 ,,	1·25
	5000 ,,	1·25
	10000 ,,	1·25
H_2SO_4	No H_2SO_4	4·10
	0·01 N	4·16
	0·1 N	4·14
	1·0 N	4·14
HCl	No HCl	1·10
	0·01 N	1·10
	0·1 N	1·08
	1·0 N	1·11

(ii) for routine use of the method an extraction time of 20 minutes may suffice, if relative standards are used for the preparation of the analysis curves.

In the latter case, normal routine samples of known copper content can be used as standards. The advantage of this method is that the standards and unknown samples are subjected to the same chemical treatment.

TABLE III

Influence of extraction time on analytical values.

Samples	Concentration of Cu based on mine chemical values for ores, % Cu	Extraction time for atomic absorption, (min)	Atomic absorption values, % Cu	% Difference between chemical and atomic absorption values
426	19·6	5	15·5	—21·1
3677	27·5		13	—52·9
3685	30·64		22·8	—25·5
				Average —32·2
426	19·6	10	17·5	—10·9
3677	27·5		25	— 9·1
3685	30·64		27·44	—10·5
				Average —10·2
426	19·6	20	18·5	— 5·7
3677	27·5		26·1	— 5·2
3685	30·64		28·54	— 6·7
				Average — 5·9
426	19·6	40	19·4	— 1·02
3677	27·5		25·7	— 6·71
3685	30·64		29·14	— 4·88
				Average — 4·20
426	19·6	Treatment A	19·6	— 0·135
3677	27·5	60	26·6	— 3·27
3685	30·64		29·5	— 3·83
				Average — 2·41
426	19·6	Treatment B	18·3	— 6·39
3677	27·5	60	27·9	+ 1·35
3685	30·64		30·38	— 0·84
				Average — 1·9

Treatment A: Ores dissolved directly and treated for 60 min.
Treatment B: Ores ignited first in porcelain crucible then treated as in A.

RESULTS

From the analytical curve illustrated in Fig. 1, it is evident that the linear portion of the curve extends to approximately 30 p.p.m. of copper. Above this value accurate results are still obtainable, but as concentrations become higher, they become less reproducible. The lower limits of analysis are limited by statistical fluctuations inherent in the apparatus.

From Table IV it can be seen that a concentration of 0·1 p.p.m. of copper can be detected. At this concentration the coefficient of variation is, however, above 10%. From 1 to 50 p.p.m. the average coefficient of variation is 1·76%, while at about 100 p.p.m. this value increases to about 3%.

TABLE IV

The change of coefficient of variation with different concentrations of copper solution

Concentration of Cu in solution, p.p.m.	Coefficient of variation on 5 repeat analyses
0·106	11·8 %
0·128	14·3 %
0·182	10·1 %
0·32	8·4 %
0·44	9·7 %
0·68	5·7 %
1·19	3·80%
1·88	2·31%
2·4	1·16%
2·6	2·60%
3·3	1·20%
4·5	1·69%
9·5	0·80%
19·03	1·40%
38·0	1·07%
47·8	2·59%
96·94	2·91%

When analysing solutions with high copper concentrations, dilutions have to be made. Personal error in measurement is magnified under these circumstances. Very concentrated solutions should also be avoided as these gave consistently low readings. This is probably due to poor spraying in the atomiser.[7]

The day to day reproducibility of the analytical curve is good, provided that all components are adjusted to optimum conditions.

Information in connection with the accuracy of the method may be gained from the results tabulated in Tables V, VI and VII. The chemical values are based on results of a standard chemical method[8] using the iodide-thiosulphate titration with starch as indicator. From these results the following may be concluded:

(i) Using a 20-minute extraction procedure and relative standards, copper concentrations in ores can be determined with an accuracy of 5·3%. This accuracy seems satisfactory when compared with the results obtained by the two chemical methods.

(ii) Using absolute standards, low values are recorded for high copper concentrations. The X-ray fluorescent method, however, gives results which are in agreement with the atomic absorption results. The accuracy of the method under these conditions is $\pm 6{\cdot}2\%$ for copper concentrations varying from 0·18% to 24% copper.

(iii) The atomic absorption method seems especially suitable for the determination of copper in ores with concentrations varying from 0·1% to 5% when absolute standards are used. With proper extraction techniques, the results given in Table VII seem to indicate that with the use of relative standards, copper concentrations as high as 25% can very satisfactorily be determined.

(iv) The chemical method as used at the mines seems unreliable for low copper concentrations.

TABLE V

Comparison of chemical analysis of ores and atomic absorption analysis of solutions obtained with 20 minute extraction using relative standards. Results given in percentage copper

Sample No.	C.S.I.R. chemical values	Atomic absorption values (rel. stds)	Percentage difference between chemical and atomic absorption values
1	24·18	24·18	0
2	19·58	19·58	0
3	9·58	8·81	— 8·04
4	4·16	4·42	+ 6·25
5	4·12	4·00	+ 2·91
6	3·34	3·67	+ 9·88
7	2·70	2·80	+ 3·70
8	2·38	2·30	— 3·36
9	1·95	1·95	0
10	0·81	0·76	— 6·17
11	0·54	0·595	+10·19
12	0·37	0·35	— 5·41
13	0·26	0·285	+ 9·62
14	0·21	0·20	— 4·76
15	0·18	0·17	— 5·56

Percentage standard deviation = 5·28

TABLE VI

*Comparison of results obtained with different analytical methods. All atomic absorption results were obtained with the use of absolute standards. Results are given in percentage copper. Values marked * were not included in the calculation of standard deviation*

Extraction time	Atomic absorption values		X-Ray fluorescence values	C.S.I.R. chemical values	Mines chemical values	Percentage difference of 40 min. extraction atomic absorption values from C.S.I.R. chemical values	Percentage difference between C.S.I.R. and Mines chemical values
	20 min	40 min	40 min				
Sample No.							
1	22·6	23·78	22·81	24·18	24·69	— 1·65	— 2·11
2	18·1	18·43	18·0	19·58	19·77	— 5·87	— 0·97
3	7·63	9·06	9·48	9·58	9·57	— 5·43	+ 0·10
4	3·59	3·95	3·5	4·16	4·15	— 5·05	+ 0·24
5	3·97	4·01		4·12	3·99	— 2·67	+ 3·16
6	3·40	3·25		3·34	3·19	— 2·69	+ 4·49
7	2·59	2·57		2·70	2·6	— 4·81	+ 3·70
8	2·12	2·15		2·38	2·35	— 9·66	+ 1·26
9	1·87	1·82		1·95	1·86	— 6·67	+ 4·62
10	0·773	0·83		0·81	0·84	+ 2·47	— 3·70
11	0·564	0·60		0·54	0·69	+11·11	—27·78*
12	0·339	0·35		0·37	0·45	— 5·41	—24·32*
13	0·262	0·25		0·26	0·35	— 3·85	—34·62*
14	0·206	0·23		0·21	0·22	+ 9·52	— 4·76
15	0·177	0·186		0·18	0·19	+ 3·33	— 5·55
			Percentage standard deviation			6·23	3·56

TABLE VII

Comparison of results obtained by chemical analysis with those from atomic absorption using a standard chemical extraction method[5]

Sample	Chemical values	Atomic absorption values	% Difference
1	24·18	23·4	—3·23
2	19·58	18·6	—5·01
3	9·58	9·22	—3·76
4	4·16	3·99	—4·09
5	4·12	3·94	—4·37

Percentage standard deviation = 4·62%

CONCLUSION

It is evident from the results given in this paper that atomic absorption spectroscopy provides a relatively quick method for the analysis of copper in solutions and in materials containing copper that can be brought into solution. Analysis of copper ores, concentrates and tailings can be done satisfactorily for production control using a 20-minute extraction.* For accurate analytical results, atomic absorption measurements at two different concentration values are recommended. Satisfactory results were also obtained using the Zeiss spectrometer with the Hilger Atomic Absorption Attachment.

Thanks are due to Messrs. Hilger and Watts for the loan of the Uvispek spectrometer, to Misses M. C. Maskew and R. E. Rethemeyer, Mrs. C. J. C. Bothma and Messrs. E. J. de Villiers and R. P. M. Procter, of this Laboratory, for technical assistance; to Dr. A. J. Rossouw, of Rand Mines, Ltd. for his help with the X-ray fluorescence results and to Dr. J. N. van Niekerk, of this Laboratory, for the ore samples.

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*This extraction time may possibly be reduced by 5 minutes if the platinum crucibles are slightly embedded in a sand bath.

A STUDY OF THE ANIONIC EXCHANGE BEHAVIOUR OF THE VANADIUM(IV) THIOCYANATE COMPLEX. SEPARATION OF VANADIUM FROM ALUMINIUM

by

L. D. C. BOK and V. C. O. SCHÜLER

OPSOMMING

Vanadium is bevredigend teruggehou toe 'n oplossing van vanadium(IV) in soutsuur, waarby tiosianaat-ione gevoeg is, deur 'n kolom van die uitruilingsharpuis Amberlite IRA 400 gestuur is. Die adsorpsie en die afwas, asook die geaardheid van die geadsorbeerde vanadiumtiosianaatioon, is bestudeer. 'n Analitiese skeiding van vanadium en aluminium is bereik.

SUMMARY

Vanadium was satisfactorily retained when a solution of vanadium(IV) in hydrochloric acid, to which thiocyanate ions had been added, was passed through a column of the ion exchange resin Amberlite IRA 400. Adsorption and elution studies are described, and the nature of the adsorbed vanadium thiocyanate ion has been studied. An analytical separation of vanadium and aluminium has been achieved.

INTRODUCTION

In the investigation described below an attempt has been made to separate vanadium(IV) and aluminium. On adding thiocyanate ions to a solution of vanadium (IV) an anionic thiocyanate complex is formed which can be adsorbed on an anionic exchange resin, whilst aluminium is not adsorbed in this way. Teicher and Gordon[1] have described a method for separating iron(III) from aluminium by similarly forming the anionic ferric thiocyanate complex ions and adsorbing these on an anionic exchange resin. Vanadium(IV) was chosen for this investigation as vanadium in hydrochloric acid solution is usually present in the tetravalent state.[2]

EXPERIMENTAL

Reagents.—Resin: Rohm and Haas Company—Amberlite IRA 400, effective size 0·4-0·6 mm (strongly basic anion exchanger).

Ammonium thiocyanate: Riedel-de-Haen, A. R.

Aluminium: B.D.H. Reagent Grade aluminium shavings.

Vanadium: Hopkin and Williams vanadium chloride (vanadyl) 50% w/w (standardised by direct titration with standard potassium permanganate[3]).

Hydrochloric acid: A.E. & C.I., chemically pure.

Exchange columns: The columns used, the treatment of the resin prior to use and the method of column operation have been described previously.[4]

Analytical methods. Vanadium was determined spectrophotometrically employing the method described by Crouthamel *et al.*[5] Aluminium was estimated by the volumetric EDTA procedure described by Schwarzenbach,[6] sulphur gravimetrically as barium sulphate[7] whilst chloride was determined electrometrically.[8]

RESULTS

Equilibrium experiments. Preliminary equilibrium experiments were conducted to ascertain whether the vanadium(IV) thiocyanate complex could in fact be adsorbed by Amberlite IRA 400 resin. The procedure adopted was that described by Freund and Miner[9] who equilibrated 2·0 g of oven dried resin with 100 ml of solution carrying the ions under test. The distribution coefficient is defined as:—

$$Kd \equiv \frac{\text{Amount of metal in resin phase}}{\text{Amount of metal in liquid phase}} \times \frac{\text{ml liquid phase}}{\text{g dry resin}}$$

In all cases the 100 ml solutions were 0·1M hydrochloric acid containing 1·0 millimole of vanadyl chloride and the ammonium thiocyanate concentration was varied from 0·1M to 2·0M. In addition to aqueous solutions, mixtures of water-acetone (1:1) and of water-ethyl alcohol (1:1) were used. The organo-water mixtures were investigated because of their application in spectrophotometric analysis where the organic solvent increases the optical density of solutions of coloured metal thiocyanate complexes,[10] presumably by decreasing the dissociation constant of the complexes.

The 100 ml test solutions together with 2·0 g Amberlite IRA 400 resin (chloride form) were placed in 250 ml glass stoppered Erlenmeyer flasks and allowed to stand at room temperature for three days with intermittent shaking to establish equilibrium between the resin and the liquid phases. Suitable aliquot portions were then pipetted from the supernatant liquids and the vanadium content estimated. The excess thiocyanate was first destroyed by treating the aliquot portions with aqua regia and sulphuric acid, followed by evaporation until fumes of sulphuric acid were evolved.

The results obtained (Table I) indicate that the vanadium thiocyanate complex is strongly adsorbed from the solvents investigated provided that the thiocyanate concentration is kept within the range 0·25M to 1·0M. Furthermore, there appears to be no advantage to be gained from aquo-organic solvents.

TABLE I

Values for the distribution coefficients of the vanadium(iv) thiocyanate complex in various solvents 2 g IRA 400 resin, 100 ml 0·1M HCl, 1 millimole $VOCl_2$

NH_4CNS molarity	Distribution coefficients		
	Water	Water-acetone	Water-ethanol
0·10	220	340	685
0·25	3655	1925	2450
0·50	4335	2125	2245
1·00	3220	1630	2245
2·00	2875	915	2085

Column experiments. Adsorption of the vanadium(IV) thiocyanate complex on 30 ml Amberlite IRA 400 resin columns was now attempted using aqueous solutions. The effect of the thiocyanate concentration on column adsorption from 0·1M as well as from 1·0M hydrochloric acid solutions was studied and the amount of vanadium that could be retained by such columns was determined. Columns with an internal

diameter of 1·5 cm containing 30 ml of resin, to give column heights of 17·0 cm, were employed.

(a) *The effect of thiocyanate concentration.* 50 Ml solutions were prepared containing 10 mg vanadium(IV) and having hydrochloric acid concentrations 0·1M and 1·0M respectively and ammonium thiocyanate concentrations 0·5M to 2·0M. These solutions were then passed through the resin columns, which were first flushed with 100 ml of solution having the same hydrochloric acid and ammonium thiocyanate concentration as the respective vanadium test solutions. A flowrate of 4 to 5 ml per minute was maintained and the effluents were collected in 250 ml volumetric flasks. The columns were washed with successive 20 ml portions of wash solution of the same strength as used for the preliminary flushing. Washing was continued until exactly 250 ml of effluent had been collected. Aliquot portions of the effluents were then analysed for vanadium as above. From the results in Table II it appears that vanadium(IV) can be efficiently adsorbed as an anionic thiocyanate complex from hydrochloric acid solution in at least the range 0·1M to 1·0M.

TABLE II

Effect of thiocyanate concentration on the adsorption of the vanadium thiocyanate complex

NH_4CNS Mo.arity	V in influent, mg	V in effluent, mg	Adsorption, %
(a) 0·1M HCl			
0·50	10·0	0·02	99·8
1·00	10·0	0·03	99·7
1·50	10·0	0·02	99·8
2·00	10·0	0·02	99·8
(b) 1·OM HCl			
0·50	10·0	0·03	99·7
1·00	10·0	0·04	99·6
1·50	10·0	0·03	99·7
2·00	10·0	0·04	99·6

(b) *The amount of vanadium(IV) thiocyanate complex retainable by a 30 ml resin column.* In order to determine the amount of vanadium thiocyanate complex that can be held by a 30 ml column of Amberlite IRA 400 resin, solutions containing various amounts of vanadium were passed through such columns. The hydrochloric acid concentration chosen was 0·25M, it being felt that lower concentrations would not be advantageous when separating vanadium from metals which do not form thiocyanate complexes. A thiocyanate concentration of 0·5M was employed as this was found to be the concentration at which the vanadium complex is best adsorbed from aqueous solution (see Table I).

By analysing the effluents from the above column experiments (Table III) it was found that at least 30 mg of vanadium(IV) can be adsorbed without any significant leakage. The adsorption of larger amounts of vanadium was not attempted because the column carrying 30 mg of vanadium had only about 3 cm of clear resin

remaining at the bottom, the upper portion being green in colour due to the adsorption of the complex.

TABLE III

Adsorption of vanadium(iv) thiocyanate complex by 30 ml resin columns from 0·5M NH_4CNS/0·25M HCl

Vanadium in influent, mg	Vanadium in effluent, mg	Adsorption, %
10·0	0·03	99·7
15·0	0·04	99·7
20·0	0·03	99·9
30·0	0·04	99·9

(c) *Elution of vanadium from the column.* Several elutriants were tried in an attempt to find a rapid means of removing the adsorbed vanadium complex from the columns. The elutriants tested included: water, 0·25M hydrochloric acid, 5M hydrochloric acid, 10M hydrochloric acid, M/10 sodium hydroxide and 2M sodium hydroxide.

Solutions containing 20 mg of vanadium(IV) in 0·5M ammonium thiocyanate/0·25M hydrochloric acid were prepared and passed through 30 ml resin columns which had previously been flushed with 0·5M ammonium thiocyanate in 0·25M hydrochloric acid. After the sorption step, the columns were washed with this flushing solution. The elutriants were then passed through at a rate of 3 to 4 ml per minute and successive 100 ml portions of the eluates were collected in 100 ml volumetric flasks. The vanadium content of the eluates were determined and the results appear in Table IV.

TABLE IV

Elution of the vanadium(iv) thiocyanate complex with various elutriants

Elutriant:	H_2O	0·25M HCl	5·0M HCl	10M HCl	M/10 NaOH	2M NaOH
	Mg vanadium in eluates					
1st 100ml	2·24	0·01	0·01	14·8	1·65	11·1
2nd ,,	3·12	0·25	1·32	3·1	0·68	3·3
3rd ,,	1·94	1·10	4·40	1·1	0·44	2·9
4th ,,	0·77	1·72	4·82	0·4	0·41	1·3
5th ,,	0·82	2·02	3·34	0·2	0·30	0·8
6th ,,	0·57	1·58	2·33	0·1	0·35	0·5
7th ,,	0·39	1·80	1·27	<0·1	0·41	0·1
8th ,,	0·28	1·39	0·68	<0·1	0·41	<0·1
9th ,,	0·20	1·46	0·34	<0·1	0·43	<0·1
10th ,,	0·11	0·87	0·38	<0·1	0·40	<0·1
Total vanadium eluted	10·44	12·20	18·99	19·7	5·48	20·0

From the data in Table IV it appears that of the elutriants tested, 10M hydrochloric acid or 2M sodium hydroxide are the most rapid. 2M sodium hydroxide is

preferable, as the 10M hydrochloric acid soon decomposes the thiocyanate in the eluates with the liberation of sulphur. This decomposition may already occur in the resin column and hence retard or even prevent further elution. It is important to note that even distilled water will remove some of the vanadium and can thus not be used for washing the columns after adsorption of the vanadium complex if this is to be quantitatively retained.

Nature of the adsorbed complex ion. An attempt was made to determine the chemical composition of the vanadium(IV) thiocyanate complex ion adsorbed, by analysing resin portions loaded with this complex. 50 Ml solutions containing 50 mg vanadium(IV) in 0·5M ammonium thiocyanate/0·25M hydrochloric acid were slowly passed through 0·75 cm internal diameter columns containing 0·5 g resin (dry weight, chloride form), which had first been soaked in water and flushed with 0·5M ammonium thiocyanate/0·25M hydrochloric acid. After the sorption step, the resin was washed with 10 ml 0·25M hydrochloric acid and not water as this would have removed some of the adsorbed vanadium (see Table IV). The excess wash solution was removed by suction. The resin was now quantitatively washed into beakers and treated with sodium peroxide, boiled, and acidified with an excess of 5 ml nitric acid. The resin was then filtered off and washed with M nitric acid. The filtrates were collected and made up to 100 ml. The vanadium, sulphur (converted to thiocyanate), and the chloride contents were determined on suitable aliquot portions. Before the chloride could be determined, it was found necessary first to convert the vanadium present to metavanadate by treatment with sodium peroxide, neutralising with nitric acid and finally boiling with sodium bicarbonate. The total chloride capacity of the resin was determined according to the method of Kunin[11] and found to be 3·40 milliequivalents per gram of resin (dry, chloride form). The analyses of four 0·5 g resin portions loaded with the vanadium complex are given in Table V.

TABLE V

Analysis of resin loaded with vanadium(iv) thiocyanate complex

Mg vanadium/g resin	Mg chloride/g resin	Mg thiocyanate/g resin
19·15	9·22	223·6
19·23	9·22	223·0
16·58	10·64	215·2
19·50	9·22	232·6

It has been stated[12] that the complex salts of tetravalent vanadium are all vanadyl derivatives and that the chemical co-ordination number of vanadium(IV) is six. Hence two anionic vanadium(IV) thiocyanate complex ions are possible, viz.: a monovalent ion $[VO(CNS)_3{:}H_2O]^-$ or a divalent complex $[VO(CNS)_4]^=$. Knowing the exchange capacity of the resin used, it is possible from the data in Table V, to calculate the number of thiocyanate groups co-ordinated to the vanadium atoms for either the monovalent or divalent complex ion adsorbed. Assuming that any of the resin exchange capacity that is not taken up by either chloride or vanadium thiocyanate complex ions is taken up by ordinary thiocyanate ions, the number of thiocyanate groups co-ordinated to the vanadium atoms is given by the ratio:—

$$\frac{\text{moles thiocyanate not adsorbed directly}}{\text{moles vanadium adsorbed}}$$

For stoichiometry this ratio must be an integer. These calculated ratios (Table VI) indicate that either of the two complex ions are possible.

TABLE VI

Calculated number of co-ordinated thiocyanate groups

	Monovalent complex	Divalent complex
	2·87	3·88
	2·86	3·84
	2·86	3·85
	3·26	4·26
Average	2·96	3·95

Sidgwick[12] states that the complex thiocyanates of vanadyl salts are easily formed and are of the type $M_2[VO(CNS)_4]aq$. This implies that the water molecules are not co-ordinated to the vanadium atom. Furthermore, the stability of co-ordination compounds is often affected by the tendency of external ions entering the co-ordination sphere, even at the expense of materials already co-ordinated to the metal. Thiocyanate is one of the ions quoted[13] as having a pronounced tendency to do this. It is thus felt that the above considerations favour $[VO(CNS)_4]^=$ for the adsorbed vanadium(IV) thiocyanate complex ions.

Separation of vanadium from aluminium. Vanadium, when present together with aluminium, will always partly accompany aluminium while this is being separated from other elements.[2] It therefore follows that when aluminium is to be determined any vanadium present must first be removed. The better known methods to achieve this include:

(1) Precipitation of the aluminium with 8-hydroxyquinoline from an ammoniacal solution containing hydrogen peroxide.[14]

(2) Precipitation of the vanadium with cupferron.[15]

The results of the work described above indicated that an anionic exchange procedure using a solution containing thiocyanate ions should yield a good method for the separation of vanadium from aluminium. 50 Ml solutions containing 10 to 20 mg vanadium(IV) and 20 to 50 mg aluminium in 0·5M ammonium thiocyanate/0·25M hydrochloric acid were thus prepared and passed through columns of resin as described for "Effect of thiocyanate concentration". The effluents were again collected in 250 ml volumetric flasks and the vanadium as well as the aluminium content determined. It was found that the aluminium could be determined without first destroying the thiocyanate present. The endpoint, however, was more distinct if the thiocyanate was first destroyed by evaporation with aqua regia. The latter procedure was thus adopted.

Table VII shows the results obtained when using this method for separating vanadium from aluminium. It is clear that good separation of small amounts of vanadium, prior to the final estimation of aluminium, is effected.

TABLE VII

Separation of vanadium(iv) from aluminium

Influent		Effluent	
Al taken, mg	V taken, mg	Al found, mg	V found, mg
20·0	10·0	20·0	<0·01
20·0	10·0	20·0	<0·01
50·0	10·0	50·2	<0·01
50·0	20·0	50·4	<0·01
50·0	20·0	50·2	0·02
50·0	20·0	50·2	<0·01

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THE LIGHT-CATALYSED HYDROLYTIC REACTIONS OF 2,4-DINITROBENZENESULPHENYL CHLORIDE WITH A NOTE ON THE CARBONYL INFRARED ABSORPTION OF ESTER AND AMIDE DERIVATIVES OF N-PHENYLHYDROXYLAMINE

by

F. KALUZA and G. W. PEROLD

OPSOMMING

Dit word getoon dat die hidrolitiese omvorming van 2,4-dinitro-benseensulfenielchloried na 2-amino-4-nitrobenseensulfoonsuur deur 'n intramolekulêre verskuiwing van suurstof ingelei word. Die eersgevormde 2-hidroksielamino-4-nitro-benseensulfoonsuurderivaat word opvolgend na die eindproduk reduseer. Albei reaksies kan deur bestraling met lig kataliseer word en vereis die inwerking van water.

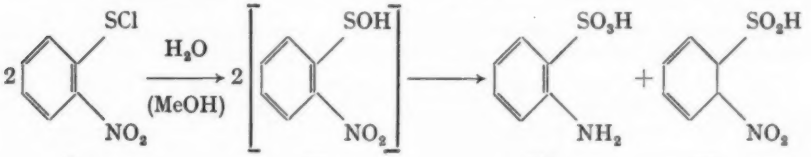
SUMMARY

The hydrolytic transformation of 2,4-dinitro-benzenesulphenyl chloride into 2-amino-4-nitrobenzenesulphonic acid is shown to commence with an intramolecular transfer of oxygen to a 2-hydroxylamino-4-nitrobenzenesulphonic acid derivative, which is then reduced to the final product. Both reaction sequences are subject to catalysis by light radiation and involve water as reactant.

2,4-Dinitrobenzenesulphenyl chloride is a very useful reagent for the characterisation of various types of organic compounds.[1] The reagent also enters into rapid reaction with a variety of small molecules.

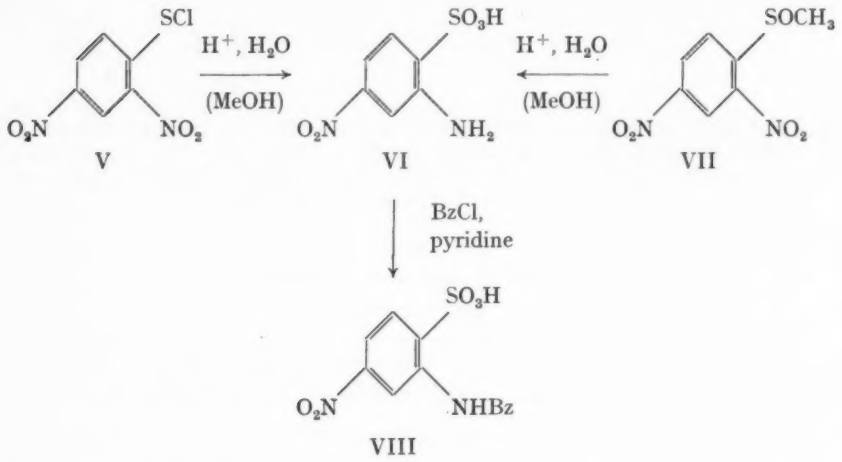
The sulphenyl chloride moiety in 2-nitrobenzenesulphenyl chloride was long ago shown[2] to react rapidly with water to give the sulphenic acid anhydride, while aqueous alkali led to the formation of the corresponding disulphide and disulphoxide. The intermediate formation of the unstable free sulphenic acid was postulated to explain the mechanism of these reactions. Exactly parallel behaviour was subsequently demonstrated for 2,4-dinitrobenzenesulphenyl chloride.[3]

A very interesting reaction, involving a larger portion of the reacting molecule, was at the time found for both the 2-nitro- and 2,4-dinitro-benzenesulphenyl chlorides respectively. Boiling in aqueous methanolic solution converted[2] 2-nitrobenzenesulphenyl chloride (I) into a mixture of orthanilic acid (III) and 2-nitrobenzenesulphinic acid (IV) in moderate yield. The decomposition of the free unstable 2-nitrobenzenesulphenic acid (II) was thought to explain this reaction.



I II III IV

Parallel behaviour was later observed[3] in the hydrolytic change of both 2,4-dinitrobenzenesulphenyl chloride (V) and the corresponding methyl sulphenate (VII) to 2-amino-4-nitrobenzenesulphonic acid (VI) in acid medium, although no sulphinic acid was then found.



The yield of the aminobenzenesulphonic acid ((III or VI), respectively) could, according to the mechanism proposed by Zincke,[2] not exceed 50%. The higher yields obtained from the related reaction on methyl 2,4-dinitrobenzenesulphenyl chloride (V) require a re-interpretation of this transformation.

Our studies on irradiated solutions of the sulphenyl chloride (V) have now shown that this reaction may be catalysed by exposure to light, and that further steps are involved, the presence of water still being essential.

A solution of 2,4-dinitrobenzenesulphenyl chloride (V) in commercial glacial acetic acid (containing 0·14% water) underwent no change when kept in the dark at 20-30° for 60 days, the reagent being quantitatively recoverable. When, however, a solution of the reagent in acetic acid containing 0·14-2·5% water was exposed to full sunlight, or to ultraviolet radiation from a quartz lamp, the colour soon darkened, while a crystalline precipitate began to form after a few hours. The product obtained after exposure for 70 hours was shown to be 2-amino-4-nitrobenzenesulphonic acid (VI), identified by comparison of its S-benzylisothiuronium salt with authentic material, by its ultraviolet absorption spectrum, as well as by its reaction with bromine water to yield 3-nitro-2,4,6-tribromoaniline[4] by substitution and by nucleophilic replacement of the sulphonic acid group. The 2-amino-4-nitrobenzenesulphonic acid was furthermore characterised as its N-benzoate (VIII) pyridinium and S-benzylisothiuronium salts.

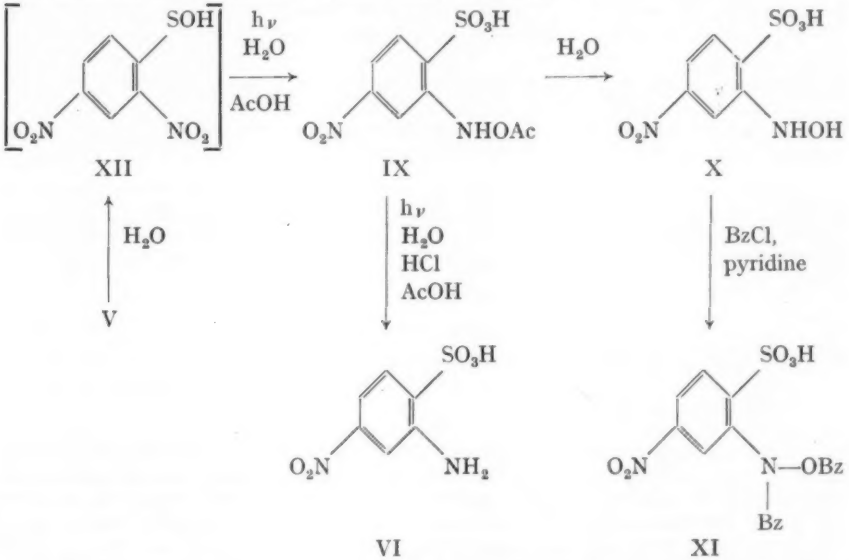
When a solution of the sulphenyl chloride (V) in anhydrous acetic acid was kept in a quartz flask in full sunlight for 35 hours, no precipitate whatsoever was obtained.

When the acetic acid solution of 2,4-dinitrobenzenesulphenyl chloride was irradiated for relatively short periods, a different crystalline product was obtained in yields of up to 64%. Although it could not be obtained completely pure, this product was identified as the unknown 2-acetoxyamino-4-nitrobenzenesulphonic acid (IX), showing strong infrared absorption at 1795 cm^{-1} (C = O in acetoxy).* It was characterised as the S-benzylisothiuronium salt.

*A number of reference compounds, derived from N-phenylhydroxylamine, were synthesized to allow the decisive identification of ester and amide carbonyl infrared absorption peaks in this study. The relevant data are summarised below in the Note appended to this paper.

The new irradiation product (IX) was hydrolysed to acetic acid and the hitherto unknown 2-hydroxylamino-4-nitrobenzenesulphonic acid (X).* This compound no more showed acetoxy carbonyl absorption in the 1800 cm^{-1} region, but now displayed hydroxyl group absorption at 3279 cm^{-1}. It was characterised as its dibenzoate (XI) pyridinium and S-benzylisothiuronium salts.

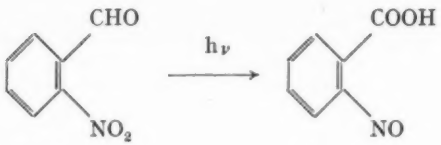
The role of 2-acetoxyamino-4-nitrobenzenesulphonic acid (IX) as an intermediate in the change leading to 2-amino-4-nitrobenzenesulphonic acid (VI) was confirmed by irradiating a suspension of (IX) in acetic acid in the presence of hydrochloric acid when the final product (VI) was readily obtained.



The overall reaction therefore involves an intramolecular rearrangement, subject to catalysis by light radiation and involving water as a reactant, of intermediately formed 2,4-dinitrobenzenesulphenic acid (XII). This leads to 2-acetoxyamino-4-nitrobenzenesulphonic acid (IX), which is finally reduced photochemically to 2-amino-4-nitrobenzenesulphonic acid (VI). This reduction involves water as a reactant, as no smooth reaction is obtained in anhydrous medium. The water presumably also accepts the photolysed oxygen atom; while the irradiated solutions do liberate free iodine from potassium iodide solution, this does not allow a clear decision as to the fate of the photolysed oxygen, because (impure) water is itself known[5] to yield hydrogen peroxide on irradiation.

The intramolecular change of (XII) to (IX) recalls the well-known Ciamician photochemical transformation[6] of o-nitrobenzaldehyde (XIII) to o-nitrosobenzoic acid (XIV), which proceeds smoothly even in the absence of solvents.,

*Potentiometric titration of this compound in aqueous solution showed $pK_1 = 2{\cdot}3 \pm 0{\cdot}1$ and $pK_2 = 7{\cdot}3 \pm 0{\cdot}1$, clearly reflecting the strong sulphonic acid group and a weak acid group respectively. As the infrared absorption spectra of compound (IX) and the salts of its N,O-dibenzoyl-derivative consistently support the presence of two free adjacent hydrogen atoms on the aromatic ring, this suggests that an arylhydroxylamine→aminophenol change occurs under the conditions of this titration. This point is presently being studied.



XIII XIV

This similarity was demonstrated by the finding that the reaction studied here also occurred on exposing the solid solvent-free reagent in (moist) air to sunlight. Many similar examples of light-induced intramolecular transport of oxygen have been collated in a recent review.[7] These without exception describe transfer[8] of oxygen from a nitro group to an acceptor group situated in an adjacent position on an aromatic ring. Furthermore, the acceptor group in nearly all these instances is at such a level of oxidation that the reaction stops after transfer of one atom of oxygen, with production of o-nitroso compounds.

In the case of the sulphenyl compounds here studied, however, the sulphur atom is at so low a level of combination that it can accept two atoms of oxygen to form a sulphonic acid derivative. The nitrogen atom in the original o-nitro* group is in this case therefore reduced to a stage beyond that of the o-nitroso group in the instances cited.

EXPERIMENTAL

M.p.s. are corrected. Infrared absorbtion spectra were taken on the Perkin Elmer Model 21 spectrophotometer, in potassium bromide dispersion except where shown otherwise.

2-*Amino*-4-*nitrobenzenesulphonic acid* (*VI*). The sulphenyl chloride (V)[9] (10·0 g) in acetic acid containing 2·5% water (200 ml) in a quartz flask, was exposed to full sunshine for 70 hours at temperatures up to 30°; the precipitate formed was filtered off daily. This material was extracted with water to give an insoluble residue (presumably bis-2,4-dinitrophenyl disulphide) (0·29 g) and a water soluble acid (VI) (5·39 g, 58% yield). This was recrystallised from water as greyish small flat prisms decomposing towards 300° (Found: C, 33·0; H, 2·9; N, 13·0; S, 14·9%; Eq. wt., 221. Calc. for $C_6H_6N_2O_5S$: C, 33·0; H, 2·8; N, 12·8; S, 14·7%; Eq. wt., 218); λ_{max} in ethanol† 238mμ (log ϵ, 4·3), λ_{min} 325 mμ (log ϵ, 2·9), λ_{max} 390 mμ (log ϵ, 3·3).

The acid (VI) (1·95 g) in hot 0·4N NaOH aqueous solution (25 ml) yielded a canary yellow sodium salt of low solubility (2·15 g) which was converted[10] to the S-benzylisothiuronium salt (3·4 g). Recrystallisation from aqueous ethanol gave the thiuronium salt as yellow scales, m.p.‡ and mixed m.p. 147·5° (Found: C, 43·8; H, 4·2; N, 14·6; S, 16·7. Calc. for $C_{14}H_{16}N_4O_5S_2$: C, 43·7; H, 4·2; N, 14·6; S, 16·7%). The reference compound was similarly obtained from the nitroaminosulphonic acid (VI) prepared[11] from 3-nitroaniline. It melted at 147·5° (Found: C, 43·7; H, 4·2; N, 14·6; S, 17·0%).

*The fact that *only* the o-nitro group is involved in this reaction supports the intramolecular mechanism proposed.

†Corresponding values for 3-nitro-aniline were λ_{max} 235 mμ (log ϵ, 4·2), λ_{min} 318 mμ (log ϵ, 2·8), λ_{max}375 mμ (log ϵ, 372).

‡Kharasch *et al.*[3] report a m.p. of 136-137° for this salt. While in our hands a double m.p. was sometimes observed (m.p. 135°, followed by resolidification and m.p. 147°), most of our preparations finally melted at 147·5°.

The acid (VI) (235 mg) warmed with bromine water[4] gave a precipitate (390 mg, m.p. 101·5°). Recrystallisation from glacial acetic acid afforded 3-nitro-2,4,6-tribromoaniline (yellow needles, m.p. and mixed m.p. 102°) (Found: C, 19·3; H, 0·8; Br, 64·1; N. 7·3. Calc. for $C_6H_3Br_3N_2O_2$: C, 19·2; H, 0·8; Br, 64·0; N. 7·5%). The reference compound, prepared directly[12] from 3-nitroaniline[13], had m.p. 102° (Found: C, 19·4; H, 0·7%).

Salts of 2-*benzamido*-4-*nitrobenzenesulphonic acid* (VIII). The acid (VI) (490 mg) on treatment with pyridine (2 ml) and benzoyl chloride (2 ml) gave the pyridinium salt of the nitrobenzamidosulphonic acid (VIII) (517 mg). Crystallisation from aqueous ethanol afforded short yellowish prisms of the pyridinium salt, m.p. 223-224° (Found: C, 53·7; H, 3·7; N, 10·8; S, 8·0. Calc. for $C_{18}H_{15}N_3O_6S$: C, 53·9; H, 3·8; N, 10·5; S, 8·0%); $\bar{\nu}_{max}$ 1678 cm^{-1} (amide C = O).

The S-benzylisothiuronium salt was obtained from the pyridinium salt in good yield[10] and was recrystallised from ethanol-water (1 : 1) as colourless needles, m.p. 176° (Found: C, 51·5; H, 4·3; N, 11·8. Calc. for $C_{21}H_{20}N_4O_6S_2$: C, 51·6; H, 4·1; N, 11·5%).

2-*Acetoxyamino*-4-*nitrobenzenesulphonic acid* (IX). The sulphenyl chloride (V)(2·0 g) in glacial acetic acid containing 0·14% water* (200 ml) in a quartz flask was exposed to full sunshine for 15 hours at temperatures up to 29°. The precipitate was filtered off, washed thoroughly with glacial acetic acid and benzene and then dried to give the impure acetoxyamino-nitrosulphonic acid (IX) (2·78 g, 59% yield) as small scales decomposing towards 300° (Found: C, 33·3; H, 2·8; N, 11·0; S, 12·5%; Eq. wt., 255.† Calc. for $C_8H_8N_2O_7S$: C, 34·8; H, 2·9; N, 10·2; S, 11·6%; Eq. wt., 276); $\bar{\nu}_{max}$1795 (C = O in acetoxy), 875 and 832 cm^{-1} (resp. one and two adjacent free H on aromatic ring).[14]

The S-benzylisothiuronium salt was obtained[10] by neutralising and reacting with S-benzylisothiuronium chloride in ice-cold solution. The product was recrystallised from aqueous ethanol as yellowish crystals, m.p. 123° (Found: C, 43·3; H, 4·4; N, 12·7; S, 14·8. Calc. for $C_{16}H_{18}N_4O_7S_2$: C, 43·4; H, 4·1; N, 12·7; S, 14·5%); ν_{max} 1748 (C = O in acetoxy), 893 and 833 cm^{-1} (1H and 2H as above.)

2-*Hydroxylamino*-4-*nitrobenzenesulphonic acid* (*X*). The crude acetoxyamino compound (IX) (1·0 g) after heating in hot ethanol-water (1 : 1) (30 ml) gave the hydroxylaminosulphonic acid (X)(670 mg), which was recrystallised from water yielding small lightly coloured scales decomposing towards 300° (Found: C, 30·7; H, 2·6; N, 12·3; S, 13·7. Calc. for $C_6H_6N_2O_6S$: C, 30·8; H, 2·6; N, 12.0; S, 13·7%). The infrared absorption spectrum no longer showed ester-carbonyl absorption near 1800 cm^{-1} but now showed hydroxyl absorption at 3279 cm^{-1}, as well as peaks at 896 and 884 cm^{-1} (1H) and 852 cm^{-1} (2H).

The acetic acid obtained in the foregoing hydrolysis was isolated in a separate experiment. Crude acetoxyamino compound (IX)(2·28 g) was powdered, dried at 72°/0·1 mm pressure for 2 hours and then refluxed in 100 ml water until solution was complete. The solution was cooled and the crystallised hydroxylamino compound (1·89 g) filtered off. The filtrate was neutralised with 0·1 N sodium hydroxide (70 ml), evaporated and reacted with p-bromophenacyl bromide (2·0 g) in ethanol (50 ml), water (15 ml) and a trace of hydrochloric acid. The product was chromatographed

*The water content was determined by Karl Fischer titration.

†The low eq. wt. may be due to the ready hydrolysis (see below), during the titration, of the acetoxyamino compound to acetic acid and the hydroxylamino compound.

over silica gel (100 g) to afford p-bromophenacyl acetate (701 mg, 33% yield), m.p. and mixed m.p. 85° (Found: C, 46·5; H, 3·5. Calc. for $C_{10}H_9BrO_3$: C, 46·7; H, 3·5%).

2-N,O-Dibenzoylhydroxylamino-4-nitrobenzenesulphonic acid (XI) salts. The hydrolysed irradiation product (X)(200 mg) in pyridine (1 ml) and benzoyl chloride (0·8 ml) gave the N,O-dibenzoate (XI) pyridinium salt (162 mg) which was recrystallised from ethanol to afford yellowish needles, m.p. 232° (Found: C, 57·3; H, 4·0; N, 8·2; S, 6·3. Calc. for $C_{25}H_{19}N_3O_8S$: C, 57·6; H, 3·7; N, 8·1; S, 6·2%); $\bar{\nu}_{max}$ 892 (weak) (1H) and 848 cm^{-1} (2H).

The pyridinium salt (as above, from 140 mg (X)) was shaken in benzene solution with 5% aqueous sodium carbonate solution to yield an insoluble sodium salt (195 mg), converted to the S-benzylisothiuronium salt (261 mg) as before. Crystallisation from aqueous ethanol afforded the pure salt as yellowish needles, m.p. 212-213° (Found: C, 55·5; H, 4·0; N, 9·6; S, 10·8. Calc. for $C_{28}H_{24}N_4O_8S_2$: C, 55·3; H, 4·0; N, 9·2; S, 10·5%); $\bar{\nu}_{max}$ 844 cm^{-1} (2H).

Conversion of 2-acetoxyamino-4-nitrobenzenesulphonic acid (IX) into 2-amino-4-nitrobenzenesulphonic acid (VI). A suspension of the acetoxyamino compound (IX) (1·21 g) in glacial acetic acid (50 ml) containing conc. aqueous hydrochloric acid* (1 ml) was exposed to full sunshine for 40 hours in a quartz flask. The temperature of the suspension rose to 55°. The precipitate was filtered off and dried (1·15 g). It (318 mg) dissolved in 3 ml warm aqueous 0·5 N sodium hydroxide solution to yield an insoluble red sodium salt (237 mg, 65% yield on IX)) which was converted as before into the yellow S-benzylisothiuronium 2-amino-4-nitrobenzenesulphonate (above), m.p. and mixed m.p. 146-147° (Found: C, 43·9; H, 4·3. Calc. for $C_{14}H_{16}N_4O_5S_2$: C, 43·7; H, 4·2%).

Solvent-free conversion of 2,4-dinitrobenzenesulphenyl chloride (V) into 2-amino-4-nitrobenzenesulphonic acid (VI). The dry powdered sulphenyl chloride (V) (1·0 g), spread on a watchglass and kept in the sun for 8 hours during one week, turned brown and sticky while hydrochloric acid fumes were given off. Extraction with benzene left an insoluble portion (480 mg), soluble in water with acid reaction and giving a sodium salt (180 mg) which was converted into S-benzylisothiuronium 2-amino-4-nitrobenzenesulphonate (176 mg), m.p. and mixed m.p. 146-147·5°.

NOTE

The carbonyl absorption in the infrared spectra of ester and amide derivatives of N-phenylhydroxylamine.

A series of acylated N-phenylhydroxylamine derivatives was prepared, in order to check the accuracy of ester and amide carbonyl infrared absorption allocations in this field.

N-Phenylhydroxylamine, m.p. 83° (lit.[15] 81°), was converted to the N,O-diacetyl derivative, m.p. 44-45° (lit. [16] 43°) which was selectively hydrolysed to the N-acetyl derivative, m.p. 68° (lit.[17] 67-67·5°).

N-Acetyl-N-phenylhydroxylamine was tosylated in the presence of pyridine to yield N-acetyl-O-tosyl-N-phenylhydroxylamine, m.p. 135°. N-Tosyl-N-phenyl-

*Hydrochloric acid was added to simulate the conditions of the overall reaction of (V)→(VI). The reduction of (IX)→(VI) also occurred in glacial acetic acid only, though the yield of the sodium salt of (VI) was then lower.

hydroxylamine,[18] m.p. 143·5° (lit.[19] 143·5°) (Found: C, 59·3; H, 5·1; N, 5·1. Calc. for $C_{13}H_{13}NO_3S$: C, 59·3; H, 5·0; N, 5·3%), was acetylated with acetic anhydride in the presence of pyridine to yield N-tosyl-O-acetyl-N-phenylhydroxylamine, m.p. 138°. N-Tosyl-N-phenylhydroxylamine with benzoyl chloride and pyridine yielded N-tosyl-O-benzoyl-N-phenylhydroxylamine, m.p. 155°.

N-Benzoyl-N-phenylhydroxylamine, m.p. 122° (lit.[20] 121-122°) (Found: C, 73·1; H, 5·3. Calc. for $C_{13}H_{11}NO_2$: C, 73·2; H, 5·2%), was tosylated as above to yield N-benzoyl-O-tosyl-N-phenylhydroxylamine, m.p. 111°.

These compounds showed strong infrared absorption bands in the 1700-1800 cm^{-1} region; these are tabulated below.

TABLE

Derivatives of N-phenylhydroxylamine, Ph-N(R_2)-OR_1

R_1*	R_2*	C=O in ester (cm^{-1})	C=O in amide (cm^{-1})	M.p.	Formula	% C		% H		% N	
						Found	Calc.	Found	Calc.	Found	Calc.
H	Ac	—	1645†	68°	$C_9H_9NO_2$	63·5	63·6	6·0	6·0	9·3	9·3
Ac	Ac	1799†	1692†	44-45°	$C_{10}H_{11}NO_3$	62·4	62·2	5·8	5·7	7·4	7·3
Tos	Ac	—	1695†	135°	$C_{15}H_{15}NO_4S$	59·0	59·0	5·0	5·0	4·9	4·6
Ac	Tos	1799	—	138°	$C_{15}H_{15}NO_4S$	58·9	59·0	5·0	5·0	4·7	4·6
Tos	Bz	—	1675	111°	$C_{20}H_{17}NO_4S$	65·3	65·4	4·9	4·7	3·9	3·8
Bz	Tos	1773	—	155°	$C_{20}H_{17}NO_4S$	65·6	65·4	4·8	4·7	3·9	3·8

*Ac = $CH_3.CO$—; Bz = $C_6H_5.CO$—; Tos = p-$CH_3.C_6H_4.SO_2$—
†These infrared spectra were taken in solution in chloroform, all others in KBr dispersion.

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GAS-LIQUID CHROMATOGRAPHY IN CAPILLARY COLUMNS. PART I—THEORY

by

P. C. HAARHOFF and VICTOR PRETORIUS

OPSOMMING

'n Streng algemene behandeling van liniêre nie-ideale gas-vloeistofchromatografie in kapillêre kolomme word gegee. Alle kolomparameters behalwe die kolomdimensies en die dikte van die vloeistoflaag word beskou as kontinue tydsafhanklike funksies van die afstand vanaf die kolominlaat. Daar word aangetoon dat die resultate geldig is mits die kolom 'n groot aantal teoretiese plate bevat.

SUMMARY

A rigorous general treatment of linear non-ideal gas-liquid chromatography in capillary columns is presented. All the column parameters other than the column dimensions and the thickness of the retentive liquid layer are treated as continuous time-dependent functions of the distance from the column inlet. The results are shown to be valid provided only that the column contains a large number of theoretical plates.

INTRODUCTION

The use of coated capillary columns for gas-liquid chromatography is now firmly established.[1] A study of such columns is important firstly because they appear to give higher efficiencies than do packed columns,[2] and secondly because they are more amenable to a rigorous theoretical study than are packed columns. Furthermore, a thorough understanding of the processes in coated capillary columns would provide a valuable pointer for the development of approximate theories of the other forms of chromatography in which the mechanism of the process is more complex.

The technique may be briefly described as follows. A suitably small gaseous sample is injected into an inert carrier gas flowing through a capillary tube on the walls of which a thin layer of liquid is deposited. The various components of the sample are distributed between the gaseous mobile and liquid stationary phases. Because their distribution coefficients will normally differ, the components will be selectively retarded by the liquid and they will form bands which move through the column at different rates. The efficiency of the separation is impaired by the fact that the bands broaden during their passage through the column. It is generally conceded[3,4] that band broadening may be ascribed to two distinct causes—longitudinal diffusion of the solute molecules in the mobile and stationary phases, and the resistance of the solute molecules to mass transfer in the mobile and stationary phases. As a result of the resistance to mass transfer the density of the solute at various points along the column cross section will deviate from the equilibrium distribution. This causes the solute to move ahead of the band centre when there is an excess of solute in the radial region of high flow velocity, while a retarding effect is produced by an excess of solute in a low flow velocity region. Longitudinal diffusion of the solute becomes more

pronounced as the diffusivity of the solute in the phases increases and also as the flow velocity is decreased. The effect of the resistance to mass transfer, on the other hand, is diminished by rapid solute diffusion and slow flow rate. It is evident that the highest column efficiency will be obtained when the operating conditions are so chosen that both the longitudinal diffusion and the resistance to mass transfer are simultaneously minimised.

A detailed study of longitudinal diffusion and of the resistance to mass transfer in coated capillary columns has been carried out by Golay.[4] An expression is obtained in which the column efficiency, in terms of the height equivalent per theoretical plate, is related to the various column parameters, e.g. gas flow rate, distribution coefficient, column diameter, etc. In the derivation of this question it has been assumed that the column parameters are constant at all points along the length of the column and also that they do not vary during the time taken by the solute band to pass through the column. In practice, these assumptions are generally approximately true. Recently, however, a certain amount of attention has been focussed on two techniques where the Golay original equation no longer holds. In the first technique very long fine bore capillary tubes are employed.[2] The pressure drop across such columns may be appreciable and since the mobile phase is compressible the gas velocity may vary significantly along the column length. Several attempts have been made to take the variation in the gas velocity into account.[4, 5, 6, 7, 8] The most elaborate of these has been carried out by Giddings *et al.*[5, 6] who adopted a statistical approach. These authors found that their results were not in good agreement with experimentally determined values.[6] Golay[4] has discussed the effect of pressure gradients in coated capillary columns in which the resistance to mass transfer in the liquid phase is negligible, and the gas velocity is at the optimum value. The method used by Golay is roughly equivalent to that of Steward *et al.*,[5, 6] but it lacks a detailed physical background.

The second technique for which the Golay equation does not apply is one in which the column temperature is programmed,[9] i.e. the column temperature is progressively changed during the passage of the solute bands through the column.

In the investigation described below an attempt has been made to develop a mathematically rigorous theory of linear non-ideal gas-liquid chromatography in coated capillary columns. The theory is more general than that given by Golay in the sense that all the column parameters, other than the column dimensions and the thickness of the stationary phase, are treated as continuous time dependent functions of the distance from the column inlet.

1. *Model and basic equations used in present study.* Consider a capillary of radius r_0*, the walls of which are coated with a thin uniform liquid layer of thickness w. The radius of the portion of the column occupied by the mobile phase is given by

$$s = r_0 - w \qquad (1)$$

* The symbols used are defined on page 113.

Under the conditions normally encountered in practice the flow of the carrier gas may be assumed to be laminar.[10] The carrier gas velocity is then given by

$$u = 2v\left(1 - \frac{r^2}{s^2}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

If a gaseous sample is now instantaneously introduced into the mobile phase at the column inlet, the mass flux of the sample in the mobile phase is given by[11]

$$\underline{j} = -\,D \text{ grad } c_1 + \underline{u}c_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

The equation of continuity is

$$\frac{\partial c_1}{\partial t} = -\text{ div } \underline{j} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

It has been assumed that the sample is sufficiently small so that the distribution isotherm will be linear. Equations (2), (3) and (4) may be combined to describe mass transfer in the mobile phase:

$$D\left(\frac{\partial^2 c_1}{\partial r^2} + \frac{1}{r}\frac{\partial c_1}{\partial r}\right) + \frac{\partial}{\partial x}\left(D\frac{\partial c_1}{\partial x}\right) = \frac{\partial c_1}{\partial t} + 2\left(1 - \frac{r^2}{s^2}\right)\frac{\partial}{\partial x}(vc_1) \quad \ldots\ldots\ldots \quad (5)$$

The ratio of the diffusivity D of the solute in the gaseous phase to the diffusivity D_1 of the solute in the liquid phase is normally greater than 10^4. Longitudinal diffusion in the liquid phase may thus be neglected.

The mass flux of the solute from the mobile to the stationary phase is given, from equation (3), by

$$j_s = -\,D\left(\frac{\partial c_1}{\partial r}\right)_{r=s} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

and from conservation of mass, by

$$j_s = \left(\frac{r_o^2 - s^2}{2s}\right)\frac{\partial \bar{c}_2}{\partial t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

as mass flow in the stationary phase is assumed to occur only in a radial direction. The ratio of the volume of the stationary phase to that of the mobile phase is given by

$$Q = (r_o^2 - s^2)/s^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

From equations (6), (7) and (8) it follows that

$$\frac{2D}{s}\left(\frac{\partial c_1}{\partial r}\right)_{r=s} = -\,Q\frac{\partial \bar{c}_2}{\partial t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Equation (9) describes the mass transfer of the solute across the gas-liquid interface.

The following equation, describing the mass transfer of solute into a flat liquid layer, has been derived by Golay[4]:

$$(c_2)_{r=s} - \bar{c}_2 = T\frac{\partial \bar{c}_2}{\partial t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

where

$$T = w^2/(3D_1) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

and

$$T\frac{\partial \overline{c_2}}{\partial t} \ll \overline{c_2} \qquad (12)$$

An equation similar to equation (10) has been shown to hold for diffusion into spherical particles,[12] provided that equation (11) is suitably modified to make allowance for the curvature of the surface. In coated capillary columns both equations (10) and (11) may be used without introducing a significant error provided that w/r_0 is smaller than about 0·3.

(2) *General differential equation describing band development.* The final form of the required solution of equations (5), (9) and (10) is an equation expressing the average concentration of the solute in the mobile phase, $\overline{c_1}$, as a function of time at the column outlet. As a first step, equations (5), (9) and (10) are reduced to a differential equation containing only one dependent variable, with x and t as independent variables. In the general case where the distribution coefficient K varies along the column, it becomes mathematically inconvenient to use $\overline{c_1}$ as dependent variable, since the total amount of the solute in the mobile phase changes during the passage of the band through the column. We therefore define a convenient parameter

$$c = \overline{c_1} + Q\overline{c_2} \qquad (13)$$

where the average concentration of the solute in the mobile phase is given by

$$\overline{c_1} = \frac{2}{s^2}\int_0^s rc_1 dr \qquad (14)$$

From equations (8) and (13) it follows that the total mass of sample per unit length of the column is related to c by

$$\rho = \pi s^2 c \qquad (15)$$

For the purpose of expressing all the dependent variables in terms of c, we begin by defining two terms which constitute a measure of the local departure from equilibrium:

$$\delta_1 = c_1 - \overline{c_1} \qquad (16)$$

$$\delta_2 = K\overline{c_2} - \overline{c_1} \qquad (17)$$

It is seen from equations (14) and (16) that

$$\int_0^r \delta_1 r dr = 0 \qquad (18)$$

The ratio of the mass of the solute in the stationary phase to that in the mobile phase, is given at equilibrium by

$$k = Q/K \qquad (19)$$

It follows from equations (13), (17) and (19) that

$$\overline{c_1} = (c - k\delta_2)/(1 + k) \qquad (20)$$

and

$$K\overline{c_2} = (c + \delta_2)/(1 + k) \qquad (21)$$

From equations (5), (9), (10), (16) and (17),

$$D\left(\frac{\partial^2\delta_1}{\partial r^2}+\frac{1}{r}\frac{\partial\delta_1}{\partial r}\right)+\frac{\partial}{\partial x}\left(D\frac{\partial\overline{c_1}}{\partial x}\right)+\frac{\partial}{\partial x}\left(D\frac{\partial\delta_1}{\partial x}\right)=\frac{\partial\overline{c_1}}{\partial t}+\frac{\partial\delta_1}{\partial t}$$
$$+2\left(1-\frac{r^2}{s^2}\right)\frac{\partial}{\partial x}(v\overline{c_1})+2\left(1-\frac{r^2}{s^2}\right)\frac{\partial}{\partial x}(v\delta_1) \quad \ldots\ldots\ldots\ldots \quad (22)$$

$$\frac{2D}{s}\left(\frac{\partial\delta_1}{\partial r}\right)_{r=s}=-Q\frac{\partial\overline{c_2}}{\partial t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (23)$$

$$\delta_2-(\delta_1)_{r=s}=-TK\frac{\partial\overline{c_2}}{\partial t} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (24)$$

On applying the operator $\frac{2}{s^2}\int_0^s r\,dr$ to each term of equation (22) to obtain an average value, we find by partial integration, when use is made of equation (18),

$$\frac{2D}{s}\left(\frac{\partial\delta_1}{\partial r}\right)_{r=s}+\frac{\partial}{\partial x}\left(D\frac{\partial\overline{c_1}}{\partial x}\right)=\frac{\partial\overline{c_1}}{\partial t}+\frac{\partial}{\partial x}(v\overline{c_1})$$
$$+\frac{4}{s^2}\int_0^s r\left(1-\frac{r^2}{s^2}\right)\frac{\partial}{\partial x}(v\delta_1)\,dr \quad \ldots\ldots\ldots\ldots \quad (25)$$

The boundary flux term may be eliminated by subtracting equation (23) from equation (25), and then using equation (13) to give

$$\frac{\partial}{\partial x}\left(D\frac{\partial\overline{c_1}}{\partial x}\right)=\frac{\partial c}{\partial t}+\frac{\partial}{\partial x}(v\overline{c_1})+\frac{4}{s^2}\int_0^s r\left(1-\frac{r^2}{s^2}\right)\frac{\partial}{\partial x}(v\delta_1)dr \quad \ldots\ldots \quad (26)$$

It is now convenient to define

$$V=v/(1+k) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (27)$$

Although equation (27) is introduced for mathematical convenience it will later be shown that the value of V at the centre of mass of the solute band is equal to the velocity of the centre of mass of the solute band. By substituting equations (20) and (27) in equation (26), an equation in terms of c, δ_1, and δ_2 is obtained:

$$\frac{\partial c}{\partial t}+\frac{\partial}{\partial x}(Vc)=\frac{\partial}{\partial x}\left[D\frac{\partial}{\partial x}\left(\frac{c}{1+k}\right)\right]-\frac{\partial}{\partial x}\left[D\frac{\partial}{\partial x}\left(\frac{k\delta_2}{1+k}\right)\right]$$
$$+\frac{\partial}{\partial x}(kV\delta_2)-\frac{4}{s^2}\int_0^s r\left(1-\frac{r^2}{s^2}\right)\frac{\partial}{\partial x}(v\delta_1)dr \quad \ldots\ldots\ldots\ldots \quad (28)$$

In order to estimate the relative importance of the various terms, certain approximations are introduced. These are later verified by equations (49) and (50), and in paragraph 6. Following Golay,[4] we shall assume that both δ_1 and δ_2 are negligibly small in comparison with $\overline{c_1}$, $K\overline{c_2}$ and $c/(1+k)$, i.e.

$$\delta_1, \delta_2 \ll \overline{c_1}, K\overline{c_2}, c/(1+k) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (29)$$

In equations (76), (81) and (83) it is proved that the concentration functions are of a Gaussian form; δ_1, δ_2, $\overline{c_1}$, $\overline{c_2}$, c and their various derivatives will thus vary from their

maximum to their minimum values in approximately the same distance, at constant time, and in the same time, at constant position. It then follows that any derivatives of δ_1 and δ_2 may be neglected, as a first approximation, in comparison with the corresponding derivatives of $\overline{c_1}$, $K\overline{c_2}$ and $c/(1+k)$.

The terms describing the departure from equilibrium may now be calculated by retaining only the largest terms in all equations. Equations (20) and (21) become

$$\overline{c_1} = c/(1+k) \quad .. .. \quad (30)$$

$$K\overline{c_2} = c/(1+k) \quad .. .. \quad (31)$$

and equations (24), (22) and (26) consequently reduce to

$$\delta_2 - (\delta_1)_{r=s} = -TK\frac{\partial}{\partial t}\left(\frac{c}{K(1+k)}\right) \quad .. .. \quad (32)$$

$$D\left(\frac{\partial^2\delta_1}{\partial r^2} + \frac{1}{r}\frac{\partial\delta_1}{\partial r}\right) + \frac{\partial}{\partial x}\left[D\frac{\partial}{\partial x}\left(\frac{c}{1+k}\right)\right] = \frac{\partial}{\partial t}\left(\frac{c}{1+k}\right) + 2\left(1 - \frac{r^2}{s^2}\right)\frac{\partial}{\partial x}(Vc) \quad (33)$$

$$\frac{\partial}{\partial x}\left[D\frac{\partial}{\partial x}\left(\frac{c}{1+k}\right)\right] = \frac{\partial c}{\partial t} + \frac{\partial}{\partial x}(Vc) \quad .. .. \quad (34)$$

By subtracting equation (34) from equation (33), we get

$$D\left(\frac{\partial^2\delta_1}{\partial r^2} + \frac{1}{r}\frac{\partial\delta_1}{\partial r}\right) = -\frac{\partial}{\partial t}\left(\frac{kc}{1+k}\right) + \left(1 - 2\frac{r^2}{s^2}\right)\frac{\partial}{\partial x}(Vc) \quad .. .. .. \quad (35)$$

The solution of this equation, under condition (18), is

$$\delta_1 = \frac{1}{24D}\left[(3s^2 - 6r^2)\frac{\partial}{\partial t}\left(\frac{kc}{1+k}\right) + \left(-2s^2 + 6r^2 - 3\frac{r^4}{s^2}\right)\frac{\partial}{\partial x}(Vc)\right] \quad .. \quad (36)$$

The value of δ_2 as calculated from equations (32) and (36) is

$$\delta_2 = -TK\frac{\partial}{\partial t}\left(\frac{c}{K(1+k)}\right) + \frac{s^2}{24D}\left[-3\frac{\partial}{\partial t}\left(\frac{kc}{1+k}\right) + \frac{\partial}{\partial x}(Vc)\right] \quad .. \quad (37)$$

The equation for c may in principle be found by substitution of equations (36) and (37) in equation (28). These calculations may, however, be greatly simplified by firstly estimating the relative importance of the various terms and discarding those that are negligible. We define a parameter by

$$\alpha = \text{maximum } [s^2v/D,\ D/v,\ (Tv)/(1+k)] \quad .. .. \quad (38)$$

Let β constitute a measure of the band width. c and its various derivatives will change from the maximum to the minimum value in a distance of the order of magnitude of β. This may be stated as

$$\frac{\partial}{\partial x}\left(\frac{\partial^{p+q}c}{\partial x^p\partial t^q}\right) \sim \frac{1}{\Delta x}\left[\Delta\left(\frac{\partial^{p+q}c}{\partial x^p\partial t^q}\right)\right] \sim \frac{1}{\beta}\frac{\partial^{p+q}c}{\partial x^p\partial t^q} \quad .. .. \quad (39)$$

where the symbol $\sim$ is used to denote an order of magnitude. The band will move along the column at a rate not differing much, if at all, from V. It then follows that

$$\frac{\partial}{\partial t}\left(\frac{\partial^{p+q}c}{\partial x^p\partial t^q}\right) \sim \frac{1}{\Delta t}\left[\Delta\left(\frac{\partial^{p+q}c}{\partial x^p\partial t^q}\right)\right] \sim \frac{V}{\beta}\frac{\partial^{p+q}c}{\partial x^p\partial t^q} \quad .. .. \quad (40)$$

By a repeated application of equations (39) and (40) one finds

$$\frac{\partial^{p+q}c}{\partial x^p \partial t^q} \sim \left(\frac{1}{\beta}\right)^p \left(\frac{V}{\beta}\right)^q c \qquad \text{(41)}$$

Let ϕ denote any one of the quantities v, V, D, T and k. Under variable conditions, the variation in ϕ along the column length at constant time, and during the experiment at constant position, will normally be of the order of magnitude of the value of ϕ at any point. It now follows by the method used to determine equation (41) that

$$\frac{\partial^{p+q}\phi}{\partial x^p \partial t^q} \sim \left(\frac{1}{L}\right)^p \left(\frac{V}{L}\right)^q \phi \qquad \text{(42)}$$

The relation between α, β, and L is best observed by introducing

$$\gamma = \text{maximum } (\alpha/\beta, \beta/L) \qquad \text{(43)}$$

i.e.

$$\alpha/\beta \leqslant \gamma \qquad \text{(44)}$$

$$\beta/L \leqslant \gamma \qquad \text{(45)}$$

$$\alpha/L \leqslant \gamma^2 \qquad \text{(46)}$$

Our previous assumptions may be conveniently generalised as

$$\gamma \ll 1 \qquad \text{(47)}$$

and the various orders of magnitude may be denoted as powers of γ. Equation (47) is verified in paragraph 6, and our previous assumptions may now be shown to be included in equation (47). Equation (12) may be written as

$$\left(\frac{\alpha}{V}\right)\left(\frac{V}{\beta}\overline{c_2}\right) \ll \overline{c_2} \qquad \text{(48)}$$

i.e.

$$\gamma \ll 1 \qquad \text{(49)}$$

From equations (36) and (37),

$$\delta_1, \delta_2 \sim (\gamma c)/(1 + k) \qquad \text{(50)}$$

so that equation (29) is satisfied.

Equation (28) may be symbolically written as

$$\frac{Vc}{\beta}(1 + 1) \sim \frac{Vc}{\beta}(\gamma + \gamma^2 + \gamma + \gamma) \qquad \text{(51)}$$

where the order of magnitude of each bracketted term in equation (28) has been separately denoted. If the first two orders of magnitude are retained, it is clear that the second term on the right hand side of equation (28) may be neglected. In each of the other terms on the right hand side, the differentiation may be carried out according to the product rule, after insertion of equations (36) and (37). In every case, it follows from equations (41) and (42) that the term of lowest order will contain derivatives of c only, and not of v, V, k, D or T. The following example serves to demonstrate this point:

$$\frac{\partial}{\partial x}(Vc) = \frac{\partial V}{\partial x}.c + V\frac{\partial c}{\partial x} \sim \frac{Vc}{L} + \frac{Vc}{\beta} \sim \frac{Vc}{\beta}.\gamma + \frac{Vc}{\beta} \qquad \text{(52)}$$

In evaluating the terms on the right hand side of equation (28), v, V, k, D and T may therefore be regarded as constants. Equations (28), (36) and (37) now become

$$\frac{\partial c}{\partial t} + \frac{\partial}{\partial x}(Vc) = \frac{D}{1+k}\frac{\partial^2 c}{\partial x^2} + kV\frac{\partial \delta_2}{\partial x} - \frac{4v}{s^2}\int_o^s r\left(1 - \frac{r^2}{s^2}\right)\frac{\partial \delta_1}{\partial x}dr \quad .. \quad .. \quad (53)$$

$$\delta_1 = \frac{1}{24D}\left[(3s^2 - 6r^2)\frac{k}{1+k}\frac{\partial c}{\partial t} + V\left(-2s^2 + 6r^2 - 3\frac{r^4}{s^2}\right)\frac{\partial c}{\partial x}\right] \quad .. \quad .. \quad (54)$$

$$\delta_2 = -\frac{T}{1+k}\frac{\partial c}{\partial t} + \frac{s^2}{24D}\left(-3\frac{k}{1+k}\frac{\partial c}{\partial t} + V\frac{\partial c}{\partial x}\right) \quad .. \quad .. \quad .. \quad .. \quad (55)$$

Substitution of equations (55) and (54) in equation (53) yields the general differential equation describing band development:

$$\frac{\partial c}{\partial t} + V\frac{\partial c}{\partial x} + \frac{\partial V}{\partial x}c = \left(\frac{D}{1+k} + \frac{s^2v^2}{48D}\frac{(1+3k)}{(1+k)^2}\right)\frac{\partial^2 c}{\partial x^2}$$
$$-\left(\frac{kvT}{(1+k)^2} + \frac{s^2v}{24D}\frac{(k+4k^2)}{(1+k)^2}\right)\frac{\partial^2 c}{\partial x \partial t} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (56)$$

(3) *Solution of the general equation in terms of distance- time coordinates.* As the total mass of solute will not affect the discussion, we impose the condition

$$\int_{-\infty}^{+\infty} c\,dx = 1 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (57)$$

on c. Let

$$z = \int_{-\infty}^{+\infty} x c\,dx \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (58)$$

designate the centre of mass of the solute band. In order to take into account the variation of v, V, D, k and T along the band, these quantities may be expanded in a series

$$\phi = \sum_{n=o}^{\infty}\frac{(x-z)^n}{n!}\left(\frac{\partial^n \phi}{\partial x^n}\right)_z \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (59)$$

about z. The subscript z denotes the value of a quantity at the centre of mass, and it is important to note that it transforms all quantities to functions of time only. For the purpose of evaluating orders of magnitude, $(x - z)$ may be replaced by β. By substituting equation (59) in equation (56) and retaining terms of the first two orders of magnitude, we get

$$\frac{\partial c}{\partial t} + \left[V_z + (x-z)\left(\frac{\partial V}{\partial x}\right)_z\right]\frac{\partial c}{\partial x} + \left(\frac{\partial V}{\partial x}\right)_z c$$
$$= \left(\frac{D}{1+k} + \frac{s^2v^2}{48D}\frac{(1+3k)}{(1+k)^2}\right)_z\frac{\partial^2 c}{\partial x^2} - \left(\frac{kvT}{(1+k)^2} + \frac{s^2v(k+4k^2)}{24D(1+k)^2}\right)_z\frac{\partial^2 c}{\partial x \partial t} \quad (60)$$

c will vanish sufficiently strongly at large distances for the relation

$$x^n\frac{\partial^p c}{\partial x^p} \quad \frac{x}{\pm\infty} \longrightarrow 0 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (61)$$

to hold for all n and p. The above relation is verified by equation (76). On applying

the operator $\int_{-\infty}^{+\infty} x dx$ to all terms of equation (60), we find by partial integration, and by using equation (61),

$$\frac{dz}{dt} = V_z = \left(\frac{v}{1+k}\right)_z \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (62)$$

When v and k do not vary along the column length, k may be interpreted as the ratio of the average time spent by each molecule in the immobile phase to the time spent in the mobile phase, during the passage of the molecule through the capillary. Equation (62) then shows that the average velocity of the solute molecule, while in the mobile phase, is equal to the average carrier gas velocity. Under variable conditions, the average transport velocity of the solute is seen to be given by the same expression, provided that the values of v and k at the centre of mass are used.

Equation (60) may now be transformed to the centre of mass coordinates, defined by

$$x_1 = x - z \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (63)$$

We shall use the symbols $\frac{\partial}{\partial t}$ and $\frac{\partial}{\partial t_1}$ to denote partial differentiation to time at constant x and x_1, respectively. The application of the operator $\frac{\partial}{\partial t_1}$ to c or its derivatives yields a term of higher order of magnitude than that resulting by the application of $\frac{\partial}{\partial t}$. We may thus assume that

$$\frac{\partial c}{\partial t_1} \sim \frac{V}{\beta}.\gamma c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (64)$$

Equation (64) is verified in paragraph 6. By the same arguments as before, this relation will also apply to the various derivatives of c. By transforming equation (60) by means of equation (63), and retaining only terms of the lowest order, we find

$$\frac{\partial c}{\partial t_1} + x_1\left(\frac{\partial V}{\partial x_1}\right)_z \frac{\partial c}{\partial x_1} + \left(\frac{\partial V}{\partial x_1}\right)_z c = \frac{V_z h_z}{2}\frac{\partial^2 c}{\partial x_1^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (65)$$

where

$$h = \frac{2D}{v} + \frac{(1 + 6k + 11k^2)}{24(1+k)^2}\frac{vs^2}{D} + \frac{2kTv}{(1+k)^2} \quad \ldots\ldots\ldots\ldots\ldots \quad (66)$$

Let $\overline{c^r}$ denote the r^{th} moment of c with respect to z, i.e.

$$\overline{c^r} = \int_{-\infty}^{+\infty} x_1^r \, c dx_1 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (67)$$

By partial integration, using equation (61), one finds

$$\int_{-\infty}^{+\infty} x_1^p \frac{\partial^{a+q} c}{\partial t_1^a \partial x_1^q} dx_1 = (-1)^q \frac{p!}{(p-q)!}\frac{d^a \overline{c^{p-q}}}{dt_1^a} \quad \ldots\ldots\ldots\ldots\ldots \quad (68a)$$

for $p \geq q$

$$= 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (68b)$$

for $p < q$

On applying the operator $\int_{-\infty}^{+\infty} x_1^2\,dx_1$ to each term of equation (65), the result is

$$\frac{d\sigma_x^2}{dt} - 2\left(\frac{\partial V}{\partial x_1}\right)_z \sigma_x^2 = h_z V_z \qquad \text{(69)}$$

when it is kept in mind that, from equation (57),

$$\overline{c_0} = 1 \qquad \text{(70)}$$

and that the variance with respect to distance from the centre of mass is given as a function of time by

$$\sigma_x^2 = \overline{c^2} \qquad \text{(71)}$$

Using equation (62), equation (69) may be written as

$$V_z \frac{d\sigma_x^2}{dz} - 2\left(\frac{\partial V}{\partial x_1}\right)_z \sigma_x^2 = h_z V_z \qquad \text{(72)}$$

The solution of equation (72), corresponding to the initial condition

$$(\sigma_x^2)_{z=0} = 0 \qquad \text{(73)}$$

is given by

$$\sigma_x^2 = \int_0^z h_{z'} \exp\left[\int_{z'}^z \left(\frac{\partial}{\partial x} \ln V^2\right)_{z''} dz''\right] dz' \qquad \text{(74)}$$

Equation (65) has to be solved under the condition

$$(c)_{z=0} = \delta(x_1) \qquad \text{(75)}$$

where $\delta(x_1)$ denotes the Dirac delta function. Assuming an approximately Gaussian function, a solution in the form of an infinite series may in principle be obtained by evaluating the successive moments of c with respect to z.[13] The Gaussian function

$$c(x, t) = (2\pi\sigma_x^2)^{-1/2} \exp\left(-\frac{(x - z)^2}{2\sigma_x^2}\right) \qquad \text{(76)}$$

is, however, found to satisfy equation (65) identically when use is made of equation (69).

(4) *The form of the elution curve.* The situation at the column exit is described by

$$c(L, t) = (2\pi\sigma_x^2)^{-1/2} \exp\left(-\frac{(L - z)^2}{2\sigma_x^2}\right) \qquad \text{(77)}$$

As the band width is, from equations (45) and (47), much smaller than the column length, σ_x^2 and V_z may respectively be replaced by $\sigma_{x_0}^2$ and V_0 during the time interval in which the solute concentration at the column exit is significant. The subscript 0 refers to the value of the various quantities at the centre of mass when the latter passes through the column exit. The relation between t and z is given, from equation (62), by

$$t = \int_0^z \frac{dz'}{V_{z'}} \qquad \text{(78)}$$

The retention time is accordingly given by

$$t_0 = \int_0^L \frac{dz'}{V_{z'}} \qquad (79)$$

By subtracting equation (79) from equation (78) we get

$$t_0 - t = \int_z^L \frac{dz'}{V_{z'}} = \frac{L - z}{V_0} \qquad (80)$$

as a lowest order approximation. Substitution of equation (80) in equation (77) yields

$$c(L, t) = (V_0)^{-1}(2\pi\sigma_t^2)^{-1/2} \exp\left(- \frac{(t - t_0)^2}{2\sigma_t^2} \right) \qquad (81)$$

where

$$\sigma_t^2 = \sigma_x^2/V_o^2 \qquad (82)$$

From equations (15), (30) and (81) the average concentration of solute in the gaseous phase at the column exit is given, in the general case where equation (57) is not applicable, by

$$\overline{c_1}(L, t) = C(2\pi\sigma_t^2)^{-1/2} \exp\left(- \frac{(t - t_0)^2}{2\sigma_t^2} \right) \qquad (83)$$

where

$$C = \frac{M}{\pi s^2(1 + k_o)V_o} = \frac{M}{\pi s^2 v_o} \qquad (84)$$

is a normalisation constant dependent upon the mass of the solute introduced into the column.

By using equations (62), (74), (79), (82) and (83) a complete description may be given of the efficiency with which various separations may be carried out. When the values of the different parameters, e.g. v (x, t) and k (x, t), are known as functions of x and t, z(t), (the position of the centre of mass of the solute band at the instant t), and t(z), (the inverse function, i.e. the time taken by the centre of mass of the solute band to reach the point z), may be calculated by solving equation (62). This is best seen by writing equation (62) as

$$\frac{dz}{dt} = \frac{v(z, t)}{1 + k(z, t)} \qquad (85)$$

The retention time is then given by

$$t_o = t(L) \qquad (86)$$

and the value of each quantity at the centre of mass may be found as a function of the position of the centre of mass, e.g.

$$V_z = \frac{v[z, t(z)]}{1 + k[z, t(z)]} \qquad (87)$$

Once V_z and h_z are known, σ_t^2 may be calculated from equations (74) and (82). The height equivalent per theoretical plate is then given by

$$H/L = \sigma_t^2/t_o^2 \qquad (88)$$

When the various operating conditions are functions of time only, as will approximately be the case when the temperature of a relatively short, wide, capillary as a whole is varied during elution, it follows from equation (85) that

$$L = \int_0^{t_0} \frac{v(t)}{1 + k(t)} dt \qquad (89)$$

from which the retention time may be determined. Using equations (74) and (82), σ_t^2 is given by

$$\sigma_t^2 = \frac{1}{V_o^2} \int_0^L h_z dz \qquad (90)$$

For techniques in which the operating factors are time-independent functions of x, t_o and σ_t^2 may be directly obtained by integration of equations (74) and (79), using equation (82):

$$t_o = \int_0^L \frac{[1 + k(x)]}{v(x)} dx \qquad (91)$$

$$\sigma_t^2 = \int_0^L \frac{[1 + k(x)]^2}{v^2(x)} h(x) dx \qquad (92)$$

In the derivation of equation (92) use has been made of the relation

$$\left(\frac{\partial}{\partial x} \ln V^2\right)_z = \frac{d}{dz} (\ln V_z^2) \qquad (93)$$

which is valid for the case in which V is time independent.

When a capillary is considered in which no variation of operating conditions occurs (this situation has been discussed by Golay[4]), the physical significance of h(x,t) becomes clear, as it follows from equations (88), (91) and (92) that h is then equal to H. The quantity h(x,t) of a column may thus be called the "local height equivalent per theoretical plate", provided that the latter term is defined as the height equivalent per theoretical plate of a second, hypothetical, column in which the column conditions are constant and equal to conditions of the first column at the point x and the instant t.

(5) *The effect of the compressibility of the carrier gas at constant temperature.* The pressure drop along the column is related at constant temperature to the average carrier gas velocity by

$$P_i^2 - P^2 = \frac{8\eta}{s^2} v_i P_i x \qquad (94)$$

and

$$vP = v_i P_i \qquad (95)$$

where the subscript i denotes the value of the various quantities at the column inlet.

Since the diffusivity of the solute in the carrier gas may be taken[14] to be inversely proportional to the gas pressure, it follows that

$$DP = D_i P_i \qquad (96)$$

Introducing the ratio of inlet to outlet pressure,

$$p = P_i/P_o \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (97)$$

it follows from equations (94) and (95) that

$$v^2\left[1 - \frac{x}{L}\left(\frac{p^2 - 1}{p^2}\right)\right] = v_i^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (98)$$

The local plate height given by equation (66) may, from equations (95) and (96), be written as

$$h = A + Bv \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (99)$$

where A and B are constant and given by

$$A = 2\frac{D_i}{v_i} + \frac{(1 + 6k + 11k^2)s^2}{24(1 + k)^2}\frac{v_i}{D_i} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (100)$$

$$B = 2kT/(1 + k)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (101)$$

For constant k, we find from equations (88), (91) and (92),

$$H = \left(L\int_o^L \frac{h}{v^2}dx\right)\Big/\left(\int_o^L \frac{dx}{v}\right)^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (102)$$

Substitution of equations (98) and (99) into equation (102) yields, after the integration is performed,

$$H = Ay_1(p) + Bv_i y_2(p) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (103)$$

where

$$y_1(p) = \frac{9(p^4 - 1)(p^2 - 1)}{8(p^3 - 1)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (104)$$

$$y_2(p) = \frac{3}{2}\frac{p(p^2 - 1)}{p^3 - 1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (105)$$

These equations are in agreement with the result derived by Giddings *et al.*[5, 6] and may be compared to the equation derived by Littlewood,[7]

$$H = A + Bv_i y_4(p) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (106)$$

where

$$y_4(p) = (2p)/(p + 1) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (107)$$

and the equation given by De Wet,[8]

$$H = A + Bv_i y_5(p) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (108)$$

where

$$y_5(p) = (8p - 3)/(5p) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (109)$$

The functions of p given by equations (104), (105), (107) and (109) have been plotted against 1/p in Fig. 1. Equations (106) and (108) do not contain any correction for A. The correction for B is given within 2% by equation (108) for $p \leqslant 5$, with a maximum error of 6·6% for $p = \infty$, and is given by equation (106) within 6% only for $p \leqslant 2{\cdot}5$, with a maximum error of 33·3% for $p = \infty$. The total maximum error possible is 11·1% with equation (108) and 33·3% with equation (106). Equation (108) appears therefore to be a more accurate approximation than equation (106). It may further be noted that the height equivalent per theoretical plate will fluctuate between 1 and 1·5 times the value of the local plate height at the column inlet.

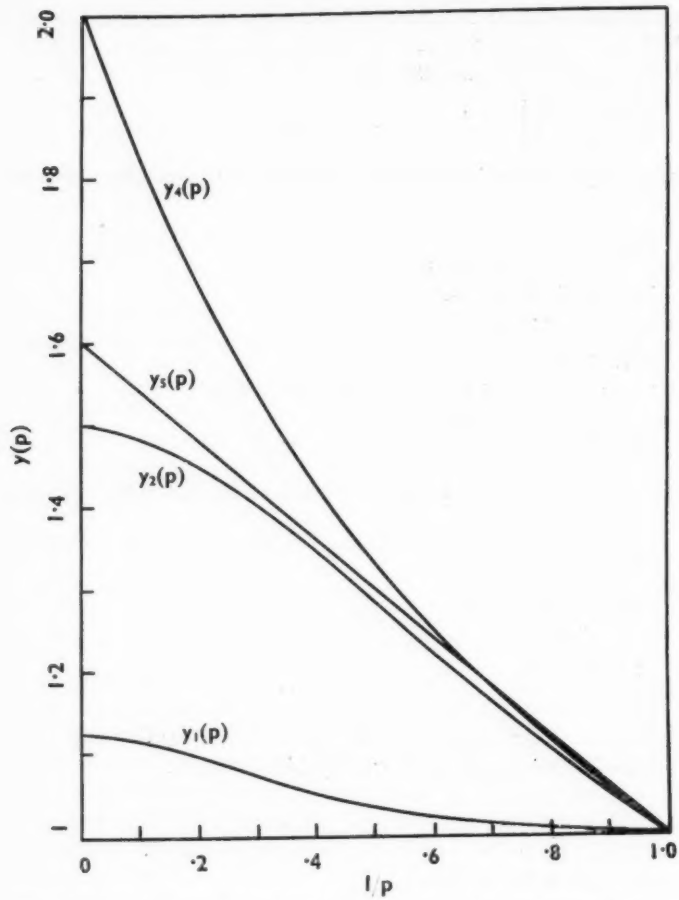

Fig. 1.—$y_1(p)$, $y_2(p)$, $y_4(p)$ and $y_5(p)$, respectively calculated from equations (104), (105), (107) and (109), plotted against 1/p.

As a measure of the efficiency of separation of a mixture of solutes, the height equivalent per theoretical plate does not take into account the influence of the retention of the solutes. This point is illustrated by a column in which k = o, for which H will have a finite value, but in which the separation of a solute mixture is impossible. This defect may be corrected[15] by the introduction of a height equivalent per theoretical plate based on the apparent retention time,

$$H_{BAR} = \frac{(1 + k)^2}{k^2} H \qquad \ldots\ldots\ldots\

which should be minimised for optimum separations. By introducing the ratio of the liquid film thickness to the capillary radius

$$\theta = w/r_0 \qquad \ldots\ldots\ldots\

(6) *Discussion of assumptions.* The assumptions made in equations (47) and (64) may now be verified. From equations (38) and (66) it is seen that

$$\alpha \sim h \qquad (120)$$

Differentiation of equation (76) with respect to time at constant x_1 yields

$$\frac{\partial c}{\partial t_1} = \frac{1}{2}\left(\frac{x_1^2}{\sigma_x^4} - \frac{1}{\sigma_x^2}\right)\frac{d\sigma_x^2}{dt}.c \qquad (121)$$

From equations (120) and (69),

$$\frac{d\sigma_x^2}{dt} \sim \alpha V \qquad (122)$$

As distances x_1 much larger than β are not of any importance, equations (121) and (122) reduce to

$$\frac{\partial c}{\partial t_1} \sim \frac{\alpha V}{\beta^2}.c \sim \frac{V}{\beta}.\gamma c \qquad (123)$$

which thus verifies equation (64).

In order to verify equation (47), β may be chosen as equal to σ_x. Equation (74) then becomes

$$\beta^2 \sim hz \qquad (124)$$

From equations (43), (120) and (124),

$$\gamma \sim \text{maximum } [(h/z)^{1/2}, (hz/L)^{1/2}] \sim (h/z)^{1/2} \qquad (125)$$

Equation (47) then becomes

$$(h/z)^{1/2} \ll 1 \qquad (126)$$

When the pressure ratio p is not very large, it follows from equations (98), (99) and (103) that

$$h \sim H \qquad (127)$$

which reduces equation (126) to

$$z/L \gg 1/N \qquad (128)$$

where N is the total number of equivalent theoretical plates. For a column with a large plate number, the approximation made in equation (47) will thus be valid for all regions except a relatively short section near the column inlet, the length of which is of the order of magnitude of H, and the influence of which will become zero as N tends to infinity. When p is large, it follows from equation (98) and (99) that equation (127), as a result of the resistance of the solute to mass transfer in the stationary phase, is not applicable in the exit region, and should be replaced in the extreme case where $p = \infty$, by

$$h \sim H(1 - x/L)^{-1/2} \qquad (129)$$

The difference between equations (127) and (129) becomes marked when

$$h/H \geq (L/H)^{1/2} \qquad (130)$$

It then follows from equations (129) and (130) that

$$L - x \ll H \qquad (131)$$

from which it may be seen that deviations from equation (127) will occur, for large N, in a relatively short section near the column exit. As previously pointed out, this effect is due to resistance of the solute to mass transfer in the stationary phase. The maximum deviation $\Delta\sigma_t$ caused by the column exit may approximated from equation (10) by

$$\Delta\sigma_t \sim T \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (132)$$

From equations (88), (99), (101) and (115) it follows that

$$\left(\frac{\Delta\sigma_t}{t_0}\right)^2 \sim \frac{1}{N}\left(\frac{\sigma_t}{t_0}\right)^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (133)$$

The influence of the region in which equation (127) is not applicable is thus negligible for large N.

On the basis of the foregoing discussion it may be concluded that the assumptions which have been made in the derivation of the general equations will not affect the accuracy of the equations provided only that the number of theoretical plates is large.

One of us (P. C. H.) is indebted to the South African Atomic Energy Board for the award of a bursary, and the other (V.P.) to Messrs. African Explosives and Chemical Industries, Ltd., and the Council for Scientific and Industrial Research, for research grants.

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LIST OF SYMBOLS

Symbol	*Dimensions*		
A	l	..	Convenient factor defined by equation (100)
B	t	..	Convenient factor defined by equation (101)
C	$ml^{-3}t$	..	Normalisation constant dependent on total mass of solute
$c(x,t)$	ml^{-3}	..	Convenient factor defined by equation (13)
$\overline{c^r}(t)$	ml^{r-2}	..	r^{th} moment of c with respect to position
$c_1(x,r,t)$	ml^{-3}	..	Concentration of the solute in the mobile phase
$\overline{c_1}(x,t)$	ml^{-3}	..	Radial average of c_1
$c_2(x,r,t)$	ml^{-3}	..	Concentration of the solute in the stationary phase
$\overline{c_2}(x,t)$	ml^{-3}	..	Radial average of c_2
$D(x,t)$	l^2t^{-1}	..	Diffusivity of the solute in the mobile phase
$D_1(x,t)$	l^2t^{-1}	..	Diffusivity of the solute in the immobile phase
H	l	..	Height equivalent per theoretical plate

H_{BAR}	l	..	Height equivalent per theoretical plate based on apparent retention
h(x,t)	l	..	Local height equivalent per theoretical plate
i	None	..	Subscript designating values at the column inlet, at constant temperature
j(x,r,t)	$ml^{-2}t^{-1}$	..	Mass flux of the solute in the mobile phase
js(x,t)	$ml^{-2}t^{-1}$	..	Mass flux of the solute from the mobile to the immobile phase
K(x,t)	None	..	Ratio of the solute concentration in the mobile phase to the concentration in the immobile phase, at equilibrium
k(x,t)	None	..	Ratio of the mass of solute in the immobile phase to the mass in the mobile phase, at equilibrium
L	l	..	Column length
M	m	..	Total mass of solute
N	None	..	Number of equivalent theoretical plates
o	None	..	Subscript denoting values at the centre of mass of the solute when the centre of mass passes through the column outlet
P(x)	$ml^{-1}t^{-2}$	..	Gas pressure at constant temperature
p	None	..	Ratio of the inlet to the outlet pressure at constant temperature
Q	None	..	Ratio of the volume of the stationary phase to the volume of the mobile phase
r	l	..	Radial distance from the centre of the column
r_o	l	..	Radius of capillary
s	l	..	Radius of mobile section
T(x,t)	t	..	Convenient factor defined by equation (11)
t,t_1	t	..	Time as measured from instant of injection of solute
t_o	t	..	Retention time
u(x,r,t)	lt^{-1}	..	Carrier gas velocity
V(x,t)	lt^{-1}	..	Velocity of the centre of mass of the solute when the latter is at (x,t)
$v(x,t)$	lt^{-1}	..	Radial average of the carrier gas velocity
$\bar{v}$	lt^{-1}	..	Longitudinal average of the carrier gas velocity, as defined in equation (115)
w	l	..	Thickness of the retentive layer
x	.l	..	Distance from column inlet

Symbol	*Dimensions*		
x_1	l	..	Distance from centre of mass of sample
y(p)	None	..	Various functions of the pressure ratio, defined in equations (104), (105), (107), (109) and (114)
z(t)	l	..	Position of the centre of mass of the sample. The subscript z denotes the value of a quantity at the centre of mass
$\alpha(x,t)$	l	..	Convenient factor defined by equation (38)
$\beta(x,t)$	l	..	Order of magnitude of the band width
$\gamma(x,t)$	None	..	Convenient factor defined by equation (43)
$\delta_1(x,r,t)$	ml^{-3}	..	Convenient factor defined by equation (16)
$\delta_2(x,t)$	ml^{-3}	..	Convenient factor defined by equation (17)
η	$ml^{-1}t^{-1}$	..	Carrier gas viscosity at constant temperature
θ	None	..	Ratio of the thickness of the retentive layer to the radius of the capillary
$\rho(x,t)$	ml^{-1}	..	Total mass of solute per unit length of the column
σ_t	t	..	Standard deviation of the concentration of the solute with respect to time at the column outlet
$\sigma_x(t)$	l	..	Standard deviation of the concentration of the solute with respect to distance
$\phi(x,t)$			Convenient factor designating v, V, D, T or k

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GAS-LIQUID CHROMATOGRAPHY IN CAPILLARY COLUMNS. PART 2. FACTORS AFFECTING THE COLUMN EFFICIENCY: THE DISTRIBUTION COEFFICIENT, THE DIFFUSIVITY OF THE SOLUTE IN THE GASEOUS AND LIQUID PHASES, AND THE THICKNESS OF THE LIQUID LAYER

by

P. C. HAARHOFF and VICTOR PRETORIUS

OPSOMMING

Die invloed van die distribusiekoëffisiënt, die diffusiwiteit van die opgeloste stof in die gas- en vloeistof-fases, en die dikte van die vloeistoflaag op die effektiwiteit van 'n kapillêre kolom is teoreties ondersoek. Die hoogte ekwiwalent aan 'n teoretiese plaat, gebaseer op skynbare retensie, word gebruik as 'n maat van die effektiwiteit. Grafiese resultate word gegee waaruit 'n skatting gemaak kan word van die effektiwiteit van die kolom wanneer die waardes van die parameters hierbo genoem, bekend is. Die bestaan van 'n optimumwaarde van die dikte van die vloeistoflaag word aangetoon. Dit blyk dat baie hoë kolomeffektiwiteite moontlik is wanneer beide die distribusiekoëffisiënt en die verhouding van die diffusiwiteit van die opgeloste stof in die gasfase tot dié in die vloeistof-fase relatief klein is.

SUMMARY

The effect of the distribution coefficient, the diffusivity of the solute in the gaseous and liquid phases, and the thickness of the liquid layer on the efficiency of a capillary column has been theoretically examined, using the height equivalent per theoretical plate based on apparent retention as a measure of the efficiency. Graphical results are given which may be used to estimate the column efficiency when the values of the parameters listed above are known. The existence of an optimum value of the thickness of the liquid layer is demonstrated. It appears that very high column efficiencies are possible when both the distribution coefficient and the ratio of the diffusivity of the solute in the gaseous phase to that in the liquid phase, are relatively small.

The efficiency with which chemical mixtures may be separated by gas-liquid chromatography in coated capillary columns is dependent on a number of factors. The following expression relating these factors to the column efficiency has been derived[1]:

$$H_{BAR} = \left[2\frac{(1+k)^2}{k^2}\frac{D_i}{v_i} + \left(\frac{1+6k+11k^2}{24k^2}\right) r_o^2(1-\theta)^2\frac{v_i}{D_i}\right] y_1(p) + \left(\frac{2\,\theta^2\, r_o^2\, v_i}{3\,k\,D_1}\right) y_2(p) \quad (1)$$

where

D_i = diffusivity of the solute in the gaseous phase at the column inlet

D_1 = diffusivity of the solute in the liquid phase

H_{BAR} = height equivalent per theoretical plate based on apparent retention[2]

K = ratio of the concentration of the solute in the gaseous phase to the concentration in the liquid phase, at equilibrium

k = ratio of the mass of the solute in the liquid phase to the mass in the gaseous phase, at equilibrium.

p = ratio of the inlet to the outlet pressure

r_o = radius of the capillary

v_i = radial average of the carrier gas velocity at the column inlet

θ = ratio of the thickness of the liquid layer to the capillary radius

and
$$y_1(p) = \frac{9(p^4 - 1)(p^2 - 1)}{8 \quad (p^3 - 1)^2} \quad .. \quad .. \quad .. \quad .. \quad (2)$$

$$y_2(p) = \frac{3p(p^2 - 1)}{2 \ (p^3 - 1)} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3)$$

$$k = \frac{2\theta - \theta^2}{(1 - \theta)^2 K} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (4)$$

Equation (1) may be used to study the way in which the column efficiency will change under a variety of experimental conditions and also to determine the experimental conditions which should be used to give the best possible separation of a particular mixture. The best method of doing this is to assign to each parameter in equation (1) a value chosen from the range of possible values which might be encountered in practice, and to calculate the column efficiency in each case. It is obvious from equation (1) that a very large number of sets of values of the parameters is possible. The method is further complicated by the fact that many of the parameters are mutually interdependent so that the value of one parameter cannot, in general, be changed without affecting the values of one or more of the other parameters at the same time. The relationship between mutually dependent parameters is also frequently complex and sometimes even unknown. A complete description of the effect, on the column of efficiency, of every possible value of each parameter, would obviously become excessively laborious.

In order to reduce the number of calculations, whilst at the same time retaining the widest possible range of parametric values, the parameters may be treated as dimensionless groups, as follows:

We define

$$Y = H_{BAR}/r_o \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (5)$$

$$X = v_i r_o/D_i \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (6)$$

Substitution of equations (5) and (6) in equation (1) yields

$$Y = (A/X + BX)\, y_1(p) + CXy_2(p) \quad .. \quad .. \quad .. \quad .. \quad .. \quad (7)$$

where

$$A = 2(1 + k)^2/k^2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (8)$$

$$B = \frac{(1 + 6k + 11k^2)(1 - \theta)^2}{24k^2} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (9)$$

$$C = \frac{2}{3}\frac{\theta^2}{k}\frac{D_i}{D_1} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (10)$$

Equation (7) is simpler for the present purpose than is equation (1) in that values only of X and not of v_i, r_o and D_i separately, need be considered. A further simplification of equation (7) may be made by ignoring the pressure correction terms, viz.

$$Y = A/X + BX + CX \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (11)$$

It follows from equations (2) and (3) that the first two terms in equation (11) can never differ by more than 11·1% from the corresponding terms in equation (7), and the third term never by more than 33·3%. Equation (11) thus gives a precise description of the processes in short, relatively wide-bore capillary columns as well as providing a description of the general trends in long, relatively narrow capillary columns. Y is given by equation (11) as a function of only four independent variables, i.e. X, K, θ and D_i/D_1. A comprehensive study of the effect of various values of these parameters on H_{BAR} is now possible. It should be noted that this is only true when the equation for H_{BAR} is expressed in terms of the values of the parameters which pertain to the column inlet.

It follows from equations (5), (6) and (11) that, at constant K, θ, D_i, D_1 and r_o, there is an optimum value of the carrier gas velocity

$$(X)_{opt} = (v_i\, r_o/D_i)_{opt} = \sqrt{A/(B + C)} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (12)$$

for which H_{BAR} will be a minimum,

$$(Y)_{opt\ X} = (H_{BAR}/r_o)_{opt\ v} = 2\sqrt{A(B + C)} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (13)$$

As D_i is dependent on the inlet column pressure, the optimum value of v_i is obtained by varying the gas pressure at the column outlet. From equation (13) it may be seen that the minimum value of H_{BAR} is directly proportional to r_o when K, θ and D_i/D_1 are kept constant, and is independent of the absolute values of the diffusivities of the solute in the mobile and stationary phases. Higher efficiencies will thus be realised with narrow than with wide capillary columns. The optimum flow velocity of the carrier gas is proportional to $1/r_o$ when K, θ, D_i and D_1 are kept constant, and narrow capillaries are thus further desirable from the point of view of rapid analyses. It follows from the above discussion that the effects on H_{BAR} of varying K, θ, D_i and D_1 at constant r_0, and of varying r_o at constant K, θ, D_i and D_1, may be superimposed upon each other, and r_o may thus be regarded as a constant in the work which follows.

The following hypothetical values of the parameters are representative of the range of possible values likely to occur in practice:

K $= 0{\cdot}001, 0{\cdot}01, 0{\cdot}1, 1$
$D_i/D_1 = 10^3, 10^5, 5 \times 10^5$
$\theta = 0{\cdot}002$ to $0{\cdot}3$.

Equations (8), (9), (10) and (11), and values of the parameters chosen from the above list, have been used to calculate Y for various values of X. The results are shown in Figs. 1-3. The minimum value of Y for each value of K and D_i/D_1 listed above has been calculated from equation (13) for various values of θ (Fig. 4).

The results in Figs. 1-3 show that the optimum carrier gas velocity increases as the resistance of the solute to mass transfer in the liquid phase is lowered, at

constant K and D_i, by decreasing the percentage of liquid and/or by increasing the diffusivity of the solute in the liquid phase. This effect is marked in all cases except when K and D_i/D_1 are both very small and may be explained as follows. It is apparent from equations (11) and (12) that, when the ratio of (B + C) to A is small, the influence of the solute resistance to mass transfer (BX and CX) becomes of the same order of magnitude as that of the longitudinal diffusion (A/X) only at relatively high carrier gas velocities. Equations (10) and (12) show that high optimum carrier gas velocities also result for large values of the diffusivity D_i of the solute in the mobile phase; the minimum value of H_{BAR}, however, becomes larger when D_i/D_1 is increased (Fig. 4). The time taken for an analysis may thus be more profitably reduced by employing large values of D_1 than by increasing D_i. When K is decreased while θ, D_i and D_1 are kept constant, the optimum carrier gas velocity decreases slowly for small values of θ and D_i/D_1, while the opposite is true for larger values of θ and D_i/D_1.

The time for analysis may also be shortened by increasing the gas velocity beyond the optimum value. However, it is evident from Figs. 1-3 that the column efficiency is at the same time decreased. This decrease may be determined by expressing H_{BAR} and v_i in terms of their optimum values, as follows: Let

$$(H_{BAR})_q = H_{BAR}/(H_{BAR})_{opt\ v} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (14)$$

$$\text{and } v_q = v_i/(v_i)_{opt} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (15)$$

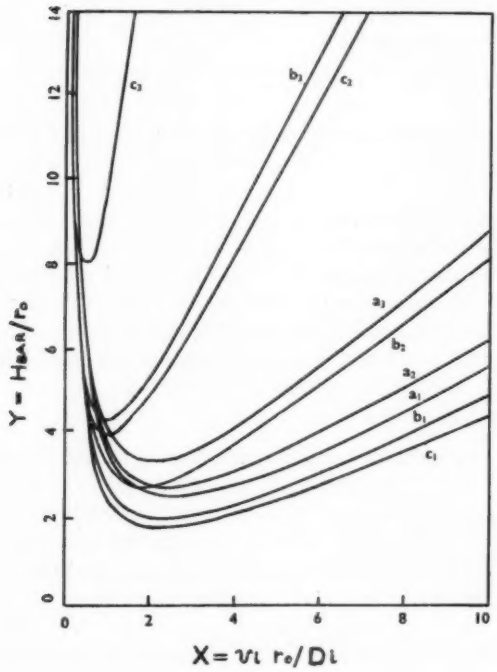

FIG. 1—The influence of the inlet gas velocity on the height equivalent per theoretical plate based on apparent retention, for K = 0·001 and the following values of θ and D_i/D_1:

D_i/D_1	θ 0·002	0·01	0·05
5×10^{-5}	a_3	b_3	c_3
10^{-5}	a_2	b_2	c_2
10^{-3}	a_1	b_1	c_1

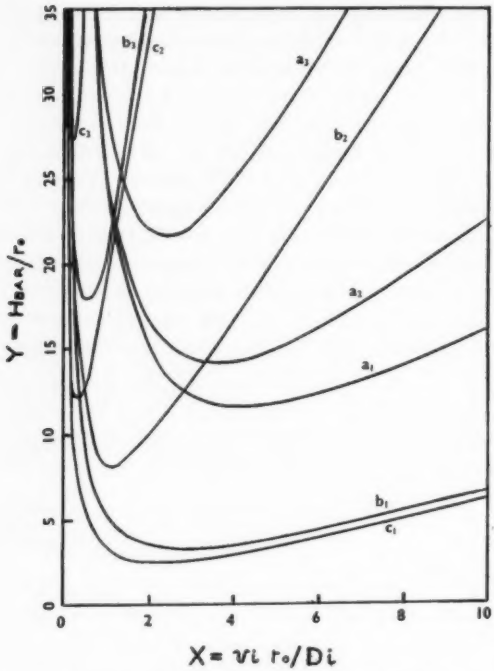

FIG. 2—The influence of the inlet gas velocity on the height equivalent per theoretical plate based on apparent retention, for K = 0·01 and the following values of θ and D_i/D_1:

	θ 0·002	0·01	0·05
5×10^5	a_3	b_3	c_3
D_i/D_1 10^5	a_2	b_2	c_2
10^3	a_1	b_1	c_1

From equations (11), (12), (13), (14) and (15) a particularly simple equation is found, viz.:

$$(H_{BAR})_q = (1/2)\,(1/v_q + v_q) \qquad (16)$$

from which it follows that an increase of the carrier gas velocity by a certain fraction of the optimum carrier gas velocity will necessarily result in an increase of H_{BAR} by a definite fraction of $(H_{BAR})_{opt\ v}$. Once a high optimum carrier gas velocity is found with a satisfactory low value of H_{BAR}, it may thus be increased by a correspondingly large value for a stipulated percentage of loss in efficiency. The precise relationship follows from equation (16). It may be noted that $(H_{BAR})_q$ changes slowly from 1 to 1·25 when v_q changes from 1 to 2, while a more rapid rate of increase $(d(H_{BAR})_q/dv_q = 0{\cdot}5)$ is found for high values of v_q.

According to Fig. 4, H_{BAR} is, in addition to r_o, dependent on θ, K, and D_i/D_1, but not on the absolute values of D_i and D_1. If $(Y)_{opt\ X}$ is plotted against θ, three distinct regions occur. For $k \lesssim 2$, i.e. $\theta \lesssim K$, both A and B increase rapidly as the liquid film thickness is made smaller, since the solutes are then not sufficiently retarded by the liquid for good resolution of the solute bands. From equations (4) and (10), C may be approximated by

$$C \doteqdot (1/3)\,\theta\,K\,(D_i/D_1) \qquad (17)$$

from which it may be seen that C becomes negligible for the region under discussion.

This is illustrated in Fig. 4, as $(Y)_{opt\ X}$ is relatively insensitive to variations in D_i/D_1 for small values of θ, especially for $K = 0{\cdot}001$. For $\theta \gtrsim 3K$ and $D_i/D_1 \gtrsim 10^4$, the resistance of the solute to mass transfer is located almost entirely in the liquid phase, and increases when more liquid is used. An intermediate region, $K \lesssim \theta \lesssim 3K$, may be distinguished, in which $(Y)_{opt\ X}$ varies very slowly with θ, and in which most of the curves in Fig. 4 exhibit an optimum percentage of liquid. The column efficiency can thus not be decreased beyond a certain limit by decreasing the thickness of the liquid layer, and consequently the resistance of the solute to mass transfer in the liquid phase. This result is somewhat surprising, since the equation derived by Golay[3], in which the efficiency is expressed in terms of the height equivalent per theoretical plate, predicts that the column efficiency increases continuously as the thickness of the liquid layer is decreased, once $k < 1$. The reason for this discrepancy lies in the employment of the height equivalent per theoretical plate as a measure of the column efficiency, instead of the more correct height equivalent per theoretical plate based on apparent retention. In Fig. 5 the minimum value $(Y)_{opt\ X,\theta}$, of $(Y)_{opt\ X}$ in the region $0{\cdot}002 \leqslant \theta \leqslant 0{\cdot}3$ has been plotted against D_i/D_1 for $K = 0{\cdot}001$, 0·01, 0·1 and 1.

Very high column efficiencies may be obtained from small values of K and D_i/D_1. The smallest H_{BAR}-value possible has been shown to be[1]

$$(H_{BAR}/r_o)_{min} = 2(11/12)^{1/2}(1-\theta) \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (18)$$

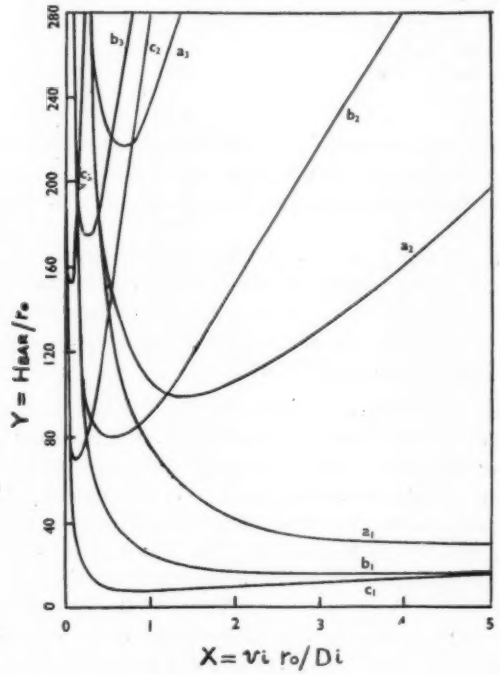

FIG. 3—The influence of the inlet gas velocity on the height equivalent per theoretical plate based on apparent retention, for K = 0·1 and the following values of θ and D_i/D_1:

D_i/D_1 \ θ	0·01	0·02	0·1
5×10^5	a_3	b_3	c_3
10^5	a_2	b_2	c_2
10^3	a_1	b_1	c_1

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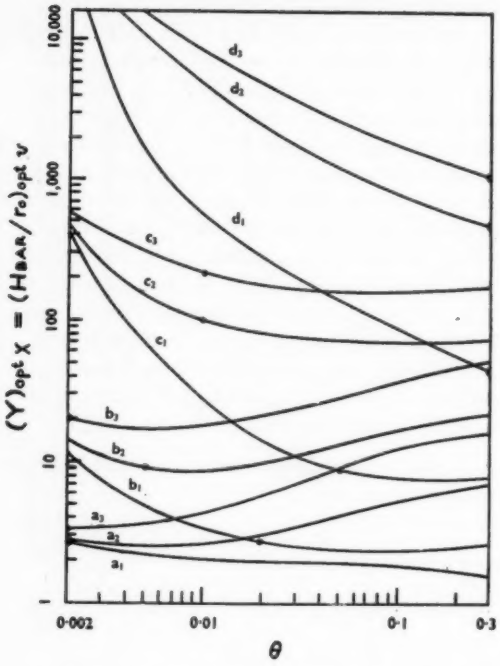

FIG. 4—The influence of the thickness of the liquid layer on the minimum height equivalent per theoretical plate based on apparent retention, for the following values of K and D_i/D_1:

	K			
	0·001	0·01	0·01	1
5×10^5	a_3	b_3	c_3	d_3
$D_i/D_1\ 10^5$	a_2	b_2	c_2	d_2
10^3	a_1	b_1	c_1	d_1

for $K = 0$, $D_i/D_1 = 0$. The factor $(1 - \theta)$ accounts for the reduction of the radius of the mobile phase by the stationary phase, but it would be impractical to reduce H_{BAR} by this means. The ultimate efficiency possible may consequently be taken as

$$(H_{BAR}/r_o)_{min} = 1{\cdot}915 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (19)$$

Extensive experimental data on the efficiency of capillary columns have not, as yet, appeared in the literature. An analysis of the results given by Golay[3] for the elution of o-xylene with helium as carrier gas and didecyl phthalate as stationary phase, shows that with $\theta = 0{\cdot}005$ and $K = 0{\cdot}00074$, a value $H_{BAR}/r_o = 8{\cdot}3$ was obtained, which approaches the best possible value within a factor 4·3.

It is clear from Figs. 4 and 5 that K and D_i/D_1 should be made as small as possible in order to facilitate favourable performance. This may best be achieved by using a liquid which interacts strongly with the solute, and has a low viscosity[4] in order to increase the diffusivity of the solute in the stationary phase. The use of elevated pressures and dense carrier gases will decrease D_i,[5] but, as previously pointed out, will result in slow optimum flow speeds. For $D_i/D_1 \lesssim 10^4$ and $K \lesssim 0{\cdot}01$ or for $K \lesssim 0{\cdot}001$ and a wide range of values of D_i/D_1, it becomes unnecessary to reduce K or D_i/D_1 any further, as this would not result in a large gain in efficiency. In this region, very thin liquid layers should be used to facilitate rapid analyses. When weakly interacting substances are analysed, i.e. $K \gtrsim 0{\cdot}1$, useful results will be obtained only

for $K \sim 0{\cdot}1$ and $D_i/D_1 \lesssim 10^4$, provided that a relatively large percentage of liquid is used. As a result of insufficient retention, solutes for which $K \sim 1$ yield impossibly high values for $(H_{BAR}/r_o)_{opt\ v}$, even when values of θ as large as 0·3 are used.

In determining the best value of θ for a given value of K and D_i/D_1, column efficiency as well as speed of analysis should be taken into account. The values of θ indicated by the circles in Fig. 4 have been chosen from these considerations. The value of the velocity of the solute band at the minimum value of H_{BAR}, $(v_i)_{opt}/(1 + k)$, multiplied by r_o/D_i in order to obtain a dimensionless factor, has been calculated for each point from equations (4) and (12). In Fig. 6 a plot is given of $(v_i)_{opt} r_o/D_i\ (1 + k)$ against K for various values of D_i/D_1.

It is seen that for $K \sim 1$, the optimum band velocity is very low, and H_{BAR} is very large. Under such conditions, there is little point in striving to obtain a reasonable efficiency: although this could be done by using extremely long columns and thick liquid layers, the time required to elute the solute would become excessive. For reasonably large values of D_i/D_1, strongly interactive solutes are eluted more slowly than are solutes which interact moderately with the solvent. This tendency would

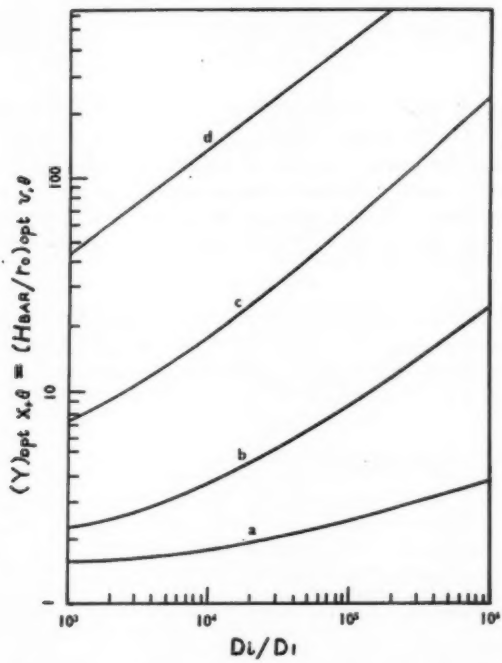

FIG. 5—The influence of D_i/D_1 on the minimum height equivalent per theoretical plate based on apparent retention, at the optimum value of θ in Fig. 4, for the following values of K: (a); K = 0·001, (b); K = 0·01, (c); K = 0·1, (d); K = 1

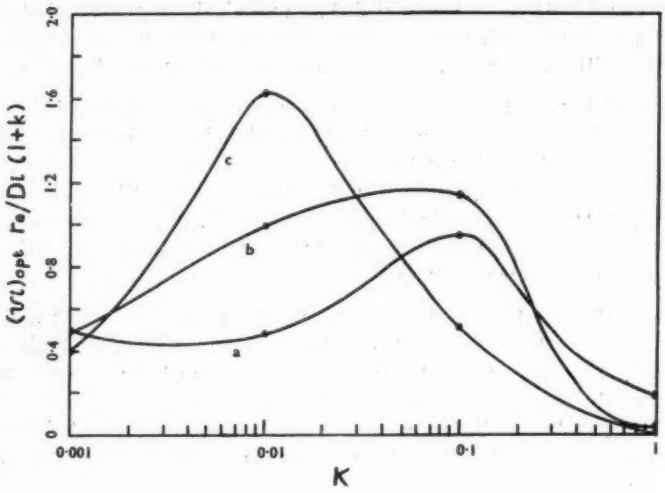

FIG. 6—The influence of the distribution coefficient on the value of the optimum band velocity, $(v_i)_{opt}/(1 + k)$, at the points indicated on Fig. 4, for the following values of D_i/D_1: (a); $D_i/D_1 = 10^3$, (b); $D_i/D_1 = 10^5$, (c); $D_i/D_1 = 5 \times 10^5$

be offset by employing values of θ smaller than the value 0·002, which has been chosen as the lower limit of θ in the present study. As a lower limit of θ will exist in practice, it would appear that the use of very low K values, when $D_i/D_1 \gtrsim 10^5$, would have the disadvantage of increasing the time of analysis without at the same time yielding a significant improvement in the column efficiency. A more satisfactory balance between these factors should thus then be obtained by using K values of roughly 0·003.

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NOTES

THE USE OF SMALL QUANTITIES OF SULPHURIC ACID AND POLYPHOSPHORIC ACID IN THE VON PECHMANN REACTION

by

B. E. BARRIS and S. S. ISRAELSTAM

Greig Gass [1] showed that the relatively large quantities of concentrated sulphuric acid used by von Pechmann [2] in his synthesis of hydroxycoumarins by the interaction of phenols and β-keto esters were unnecessary, and that only a few drops of the acid were sufficient, provided that acetic anhydride was added to take up the water formed in the reaction.

Some years ago it was found that the addition of the acetic anhydride was unnecessary and that a relatively small quantity of sulphuric acid alone was quite sufficient to give good yields of 7-hydroxy-4-methylcoumarin by heating together fifth molar quantities of resorcinol, ethyl acetoacetate and 0.1 g concentrated sulphuric acid for about 30-40 minutes at 120°C. Recently the opportunity presented itself to continue with this investigation and the formation of hydroxycoumarins from various phenols and β-keto esters using small quantities of sulphuric acid has been studied in detail. Furthermore, the use of polyphosphoric acid was also investigated. Koo [3] has shown that this reagent has certain advantages over sulphuric acid and can be used as a condensing agent in this reaction, but as with von Pechmann's use of large quantities of sulphuric acid, he used large quantities of polyphosphoric acid. Thus, for tenth molar quantities of resorcinol and ethyl acetoacetate as much as 160 g of polyphosphoric acid were used. We have found that comparable yields of coumarins are obtained using very much smaller quantities of polyphosphoric acid but longer heating is necessary than in the case of sulphuric acid. In general, better yields were obtained with sulphuric acid.

In order to find the optimum conditions for this reaction, a series of experiments was carried out, varying the quantity of condensing agent and the time of the reaction in each case. These results are summarised in the Table.

It will be noted that very good yields of coumarin were obtained in the case where "reactive" phenols (e.g. resorcinol) and "reactive" β-keto esters (e.g. ethyl acetoacetate) were condensed together, but that low yields of coumarin resulted when less "reactive" phenols (e.g. orcinol) and β-keto esters (e.g. ethyl α-methylacetoacetate) were used. In most cases the optimum temperature was found to be 120-130°C and the time of heating varied from 5 minutes to 30 minutes, depending on the weight and reactivity of the phenol and β-keto ester.

After this work had been completed, our attention was drawn to a patent by Boese [4] who had developed a method for the preparation of hydroxycoumarins also using small quantities of concentrated sulphuric acid, but using toluene as a solvent and refluxing the mixture for an hour in order to remove the alcohol and water formed in the reaction as an azeotropic mixture. Toluene is not required on the

TABLE

Preparation of hydroxycoumarins

β-Keto ester		Phenol		Coumarin formed	Conc. sulphuric acid			Polyphosphoric acid			M.P. °C		
Name	Wt. in g.	Name	Wt. in g		Wt. in g	Time of heating in mins.	% Yield	Wt. in g	Time of heating in mins.	% Yield	Found	Literature	Ref.
Ethyl aceto-acetate	2·6	Resorcinol	2·2	7-hydroxy-4-methyl				0·3	60	93	184	184	6
								1·0	30	94			
								4·0	15	94			
	13		11					1·0	60	75			
								4·0	40	87			
								8·0	30	94			
	26		22		0·1	40	100						
	3·0	Phloroglucinol	2·5	5, 7-dihydroxy-4-methyl	0·05	3	42	0·6	60	50	284	284	2
					0·4	10	80	1·2	30	80			
					1·2	5	82	5·5	15	80			
	2·4	Pyrogallol	2·0	7, 8-dihydroxy-4-methyl	0·2	10	75	0·3	30	71	233	235	7
					0·4	10	87	1·2	30	76			
	12·0		10·0		0·4	30	53						
					0·8	30	75						
	3·0	Orcinol	2·5	7-hydroxy-4, 5-dimethyl	0·4	10	57	0·6	90	36	248	250	7
					0·8	10	63	1·2	60	38			
					1·2	5	71	1·8	60	50			
								2·4	45	75			
	3·0	α-Naphthol	2·9	7, 8-benzo-4-methyl	0·8	30	74				167–9	167	7
	6·0		5·8		0·05	90	67						
	4·5	4-Chlororesor-cinol	5·0	7-hydroxy-4-methyl-6-chloro	0·05	15	52				278	280	9
					0·1	15	56						
Ethyl α-ethyl acetoace-tate	2·8	Resorcinol	2·2	7-hydroxy-4-methyl-3-ethyl	0·05	75	50	0·6	60	54	196–8	198	10
					0·4	30	70	0·9	60	64			
					0·8	30	92	2·4	30	75			
	2·5	Phloroglucinol	2·0	5, 7-dihydroxy-4-methyl-3-ethyl	0·2	30	70	0·6	60	16	216	218	11
					0·4	30	80	1·2	60	35			
								1·8	60	40			
	2·5	Pyrogallol	2·0	7, 8-dihydroxy-4-methyl-3-ethyl	0·4	30	77	1·2	15	50	218	219	12
		Orcinol	2·0	5-hydroxy-4, 7-dimethyl-3-ethyl	0·4	30	17	1·8	60	43	204	206	11
								2·4	60	58			

TABLE—*continued*
Preparation of hydroxycoumarins

β-Keto ester		Phenol		Coumarin formed	Conc. sulphuric acid			Polyphosphoric acid			M.P. °C		
Name	Wt. in g.	Name	Wt. in g		Wt. in g	Time of heating in mins.	% Yield	Wt. in g	Time of heating in mins.	% Yield	Found	Literature	Ref.
Ethyl benzoyl-acetate	3·6	Resorcinol	2·2	7-hydroxy-4-phenyl	0·05 0·2 0·4	20 20 20	58 83 87	0·6 1·8 2·4	60 30 30	63 83 90	244–5	245	2
	3·2	Phloroglucinol	2·0	5, 7-dihydroxy-4-phenyl	0·05 0·2 0·4	45 30 20	42 75 95	1·2	30	55	228	234	10
	3·2	Pyrogallol	2·0	7, 8-dihydroxy-4-phenyl	0·4	60	50	1·2 2·4	30 45	28 50	190	192	12
	3·2	Orcinol	2·0	7-hydroxy-4-phenyl-5-methyl	0·05	60	12	1·2 2·4	60 30	14 17	213	213	1
	6·6	4-Chlororesorcinol	5·0	7-hydroxy-4-phenyl-6-chloro	0·05	240	10				266	258-60	8
Ethyl α-methylaceto-acetate	13·0	Resorcinol	11·0	7-hydroxy-3, 4-dimethyl	0·15 0·20 0·30	20 20 20	45 50 51	1·0	30	18	255-6	256	2
	2·3	Phloroglucinol	2·0	5, 7-dihydroxy-3, 4-dimethyl	0·05	15	51				288	291	10
	2·3	Pyrogallol	2·0	7, 8-dihydroxy-3, 4-dimethyl	0·05	15	42				271	272	10
	2·3	Orcinol	2·0	5-hydroxy-3, 4, 7-trimethyl	0·05	45	36				250	250	11
Ethyl α-benzyl-aceto-acetate	3·0	Resorcinol	2·2	7-hydroxy-3-benzyl-4-methyl	0·05	90	57				225-7	225-6	13
	3·0	4-Chloro-resorcinol	2·0	7-hydroxy-3-benzyl-4-methyl-6-chloro	0·05	240	17				249	249	8
Ethyl α-* chloro-aceto-acetate	3·0	Resorcinol	2·0	7-hydroxy-4-methyl-3-chloro	0·05	60	90				235	236	14
	1·3	Phloroglucinol	1·0	5, 7-dihydroxy-4-methyl-3-chloro	0·05	60	75				304	306-8	7
	2·6	Orcinol	2·0	7-hydroxy-4, 5-dimethyl-3-chloro	0·05	60	30				290	295	14

* The temperature of these reactions: 94°C (on water bath).

laboratory scale. Furthermore, Boese did not list polyphosphoric acid among the condensing agents given in his patent.

The method described here has been used for some years by students for the laboratory preparation of 7-hydroxy-4-methylcoumarin and a preliminary note has already appeared [5].

Consideration has been given to the mechanism of the von Pechmann reaction in the light of these and other experiments and the results will be published elsewhere.

EXPERIMENTAL

Hydroxycoumarins. The following was the general procedure adopted:

Equimolecular quantities of the phenol and the β-keto ester were heated together with various quantities of condensing agent in an oil bath at 120°-130°C. When the reaction appeared to be complete, i.e., when either the product solidified or when no further effervescence occurred, water was added, the mixture cooled, the crude product filtered off, washed with hot water and then with a small volume of 5 per cent. ethanol. The coumarin was crystallised from 50 per cent. ethanol.

Where the product did not solidify on the addition of water, the following methods were adopted:

(a) If the product became pasty on the addition of water as in the case of 5,7-dihydroxy-4-methyl-3-ethylcoumarin, the coumarin was extracted by boiling the paste with water and allowing the solution to crystallise. This process was repeated a number of times.

(b) If an oil was formed on the addition of water and did not solidify on cooling ethanol was added drop by drop until solidification occurred.

The results of a number of experiments are summarised in the Table. Mixed melting points of the various coumarins with authentic specimens in each case showed no depression. The melting points of the crude coumarins in all cases were 2°-6°C below that recorded for the pure material.

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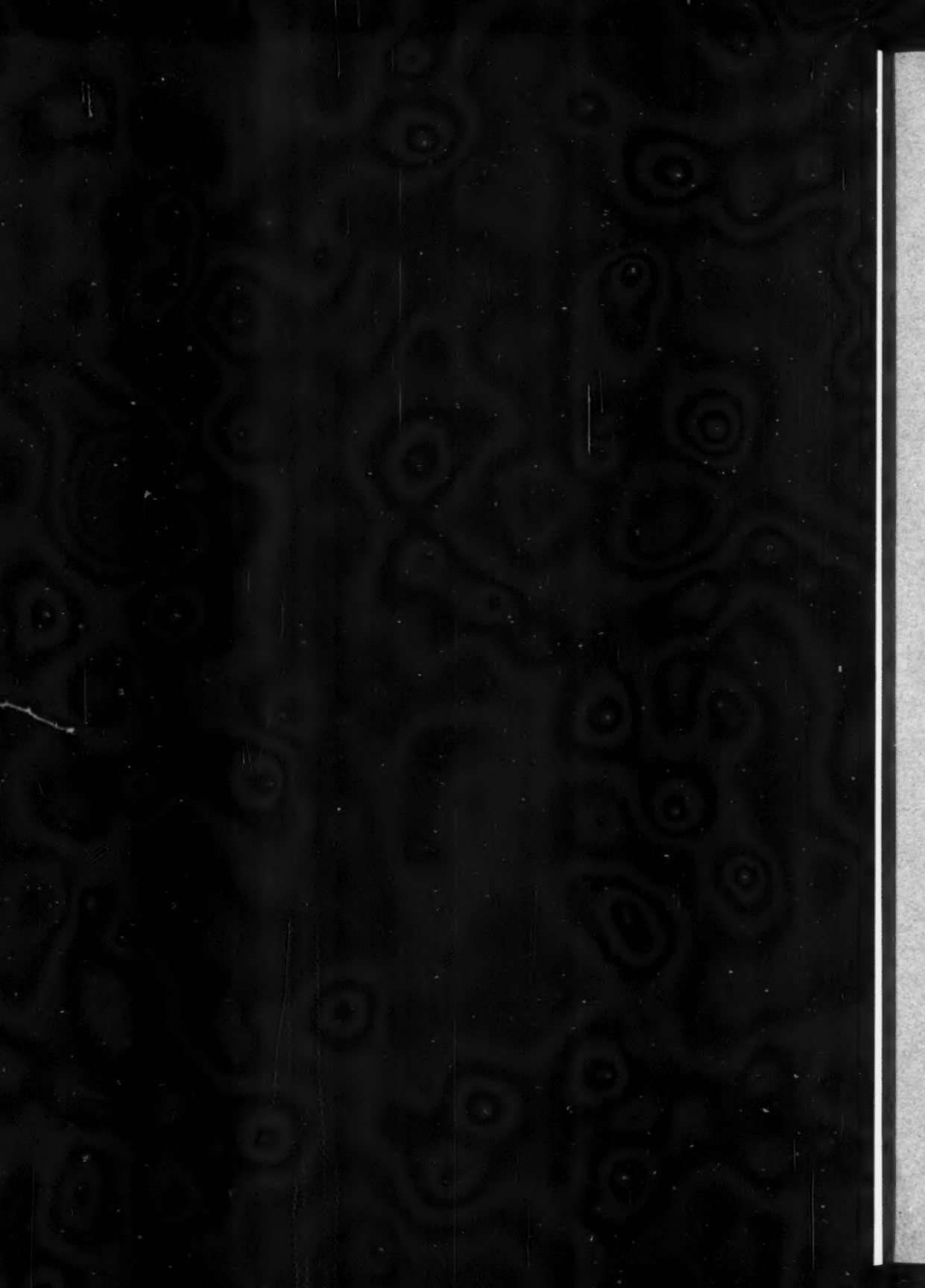

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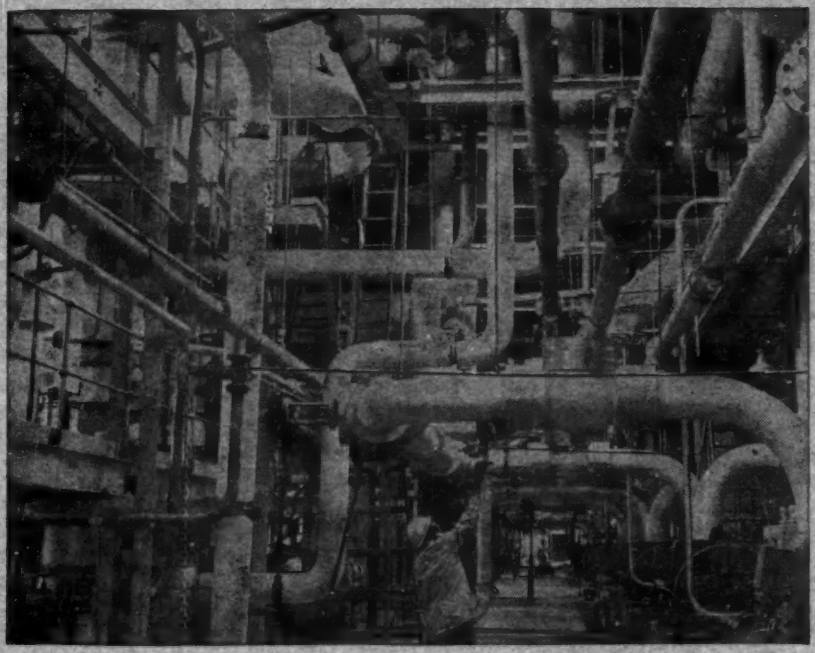

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